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ENERGY AND PRESSURE CALCULATIONS FOR METALLIC NH$_4$

LEVEL II

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It has long been known that the ammonium ion $NH_4(+)$ behaves in many ways like an alkali metal ion. This report discusses a possible transition (under pressure) from a mixture of ammonia and hydrogen ($NH_3 - \frac{1}{2}H_2$) to metallic NH_4 in the "funny sodium" form. This form may be defined as a lattice composed of metallic $NH_4(+)$ ions and s-like electrons (one per ion). The ion has the sodium Z number but only seven protons (those from N) are in the nucleus; the

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other four protons (those from the four H atoms) form a tetrahedral arrangement around the N nucleus. This tetrahedral arrangement is then approximated by a spherical shell at a radius determined by a variational calculation for the total energy of the tetrahedral ion. (The resulting radius lies well out in the ion electron cloud.) Since a Wigner-Seitz polyhedra approach is used no specific lattice structure is considered. We comment on the earlier calculation of Bernal and Massey (BM) and the more recent calculation of Stevenson. Emphasis is on the BM metallic calculation which we have essentially repeated.

The concept of exchange is described, derivation of the Fock equations is given, and the principal equation of BM (one electron outside a closed shell) is then derived from the Fock equations.

The BM equation is then solved by computer for both the no-exchange and exchange-included cases. Our (unsuccessful) attempts to reproduce the BM results for the no-exchange case are described briefly. Our calculation for the exchange-included case is then described in some detail. For this case we find the internal energy at the equilibrium volume to be about 0.5 ev higher than that obtained by BM (our value is very close to Stevenson's -5.36 ev). Stevenson's equilibrium radius is 5.35 a.u., BM's is 4.23 a.u.; we obtain 4.99 a.u., i.e., shifted considerably toward Stevenson's value. In spite of these differences in U vs V between our results and BM's, our Gibbs energy vs pressure curve is about like theirs.

If the Stevenson mixture curve for U vs V is accepted, the BM and the present metallic calculation make a transition to "funny sodium" NH_4 unlikely (at least below the Mbar region). Acceptance of the Stevenson metallic U vs V curve would make such a transition unlikely at any pressure. We consider transition to the "funny sodium" form to be unlikely; transitions to other metallic forms are probably in the Mbar (and above) range.

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I. INTRODUCTION

There has been renewed interest recently[1] in a possible transition from a mixture of ammonia and hydrogen to metallic NH_4. Chemically, the transition can be expressed by the reaction

$$2NH_3 + H_2 \rightarrow 2NH_4 \tag{1}$$
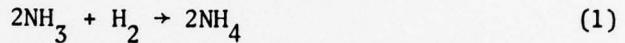
In a calculation made some years ago, Bernal and Massey[2] (BM) concluded that such a transition would occur between 60 and 140 kbar. Stevenson[1], however, concluded that the transition would not occur, at least not below 1 Mbar. (The compact metallic phase that would then form is unrelated to the low density metallic phase considered here, namely, the "funny sodium" form.)

The fundamentally correct approach to determine phase transition pressure P_t is to plot Gibbs energy G versus pressure P for each phase and define P_t as the pressure at which the two curves cross. This follows from the thermodynamic argument that $dG \leq 0$ for P,T constant so that the only place both phases can be in equilibrium is where $dG = 0$[3]. A second approach is to plot internal energy U vs volume V for each phase and then define P_t as the common tangent. Since $dG = 0$ implies $dU = TdS - PdV$ for constant P and T, $P = -dU/dV$ if the TdS/dV term can be ignored, then the common slope of the U

[1]D. J. Stevenson, Nature 258, 222 (1975).

[2]M. J. M. Bernal and H. S. W. Massey, Mon. Not. R. Astr. Soc. 114, 172 (1954).

[3]M. W. Zemansky, "Heat and Thermodynamics," McGraw-Hill (1943), p. 320.

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vs V plot is the common pressure of the G vs P plot and the two approaches are equivalent.

A number of different methods are frequently utilized to determine G (or U). Typically, the differences between these various methods consist of different approximations to the potentials and/or different requirements on the system wave functions. When one of the phases is metallic these considerations involve a decision about the "exchange" term (see below), both whether and how to include this term. Both BM and Stevenson include this effect: BM by using Hartree-Fock theory, Stevenson by using the Kohn-Sham-Slater "average exchange" which supposedly includes exchange and correlation effects in a local but self-consistent approximation. Since the latter procedure tends to give a lower metallic energy than straight Hartree-Fock, it is somewhat curious that Stevenson's NH_4 energy values are higher than those of BM. Both calculations use a "sphericized" NH_4^+ ion. Stevenson claims[4] this causes him to be about 0.1 ev high. From a rapid skimming of Chapters 10 and 11 of ref. 5, this author would have expected this to make a bigger difference.* Both calculations use a rigid r_o, the radius of the smeared out protons in the sphericized model. A flexible r_o would allow lower energy (this would be more

_____

[4] D. J. Stevenson (private communication) (Letter to Curtis Selph, Oct. 1976).

[5] J. C. Slater, "Quantum Theory of Molecules and Solids, Vol. 1," McGraw-Hill (1963).

* Note added in proof: The comments in ref. 5 are not applicable here: Slater's molecules fill the space; the NH_4^+ ions do not. Thus, sphericizing makes little difference. We thank Dr. Stevenson for pointing this out.

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important at high pressures and correcting would tend to give G **vs** P a less steep slope).[6]

Since Stevenson's paper[1] gives only a bare outline of his calculation, whereas the BM paper[2] gives a relatively complete outline of their calculation (including a tabulation of the effective potential and of the core wave functions) we have attempted to repeat the BM calculation. The plan of the present report is as follows: In the next section we discuss what is meant by "exchange". In section III the Fock equations are derived and then the principal equation of BM is obtained from the Fock equations - details of these derivations are given in the Appendices. Section IV summarizes our initial *attempts to obtain BM's U vs V curve (without exchange)*. Section V summarizes our work with exchange included. A summary of the entire report is given in Section VI.

II. EXCHANGE

Exchange is a quantum-mechanical term arising from the Pauli exclusion principle; there is no classical analog. (One can, however, give a physical interpretation to the exchange term; such an inter-

[1]D. J. Stevenson, Nature 258, 222 (1975).

[2]M. J. M. Bernal and H. S. W. Massey, Mon. Not. R. Astr. Soc., 114, 172 (1954).

[6]Stevenson (ref. 4) estimates this correction to be about 0.03 ev/ion i.e., negligible.

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pretation can be used to approximate the exchange term leading to Slater "local" exchange, etc. Since BM do not use this approximation we shall not comment further on it here.) Since we are dealing with electrons (spin = 1/2) the complete (spin and space coordinates) wave function must be anti-symmetric. This is consistent with the requirement that the probability of two fermions occupying the same state should be zero.

The essence of the origin of the exchange term can be illustrated by the following simple example: consider two electrons with the same spin but represented by two different functions f and g. The anti-symmetric wave function for the system is then

$$\Psi(1,2) = f(1)g(2) - g(1)f(2) \tag{2}$$

where (1) stands for the x,y,z coordinates of the first electron, etc.[7] The coulomb operator part of $\int \Psi^* H \Psi d\tau_1 d\tau_2$ gives:

$$\int \Psi^*(1,2)(e^2/r_{12})\Psi(1,2)d\tau_1 d\tau_2$$

$$= 2\int g^*(2)(e^2/r_{12})g(2)d\tau_2 \int f^*(1)f(1)d\tau_1 -$$

$$2\int g^*(2)(e^2/r_{12})f(2)d\tau_2 \int f^*(1)g(1)d\tau_1$$

where $\vec{r}_{12} \equiv \vec{r}_1 - \vec{r}_2$; dummy variables have been interchanged as appropriate.

---

[7]For the general, N-particle case, Ψ would be the N-particle determinant:

$$\Psi(1,2\ldots,N) = \begin{vmatrix} f_1(1) & f_1(2) & \cdots & f_1(N) \\ f_2(1) & f_2(2) & \cdots & f_2(N) \\ \vdots & \vdots & & \vdots \\ f_N(1) & f_N(2) & \cdots & f_N(N) \end{vmatrix}$$

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In determining ground-state energy via the variational procedure we add Lagrange multipliers to effectively make all the functions independent and vary, say, $f^*(1)$. In the equation for $f(1)$ the two terms above become

$$2f(1)\int g^*(2)(e^2/r_{12})g(2)d\tau_2 - 2g(1)\int g^*(2)(e^2/r_{12})f(2)d\tau_2$$

The first term is clearly the direct coulomb term and represents the potential energy of the electron associated with coordinate 1 in the field of electron 2. The second term is the "exchange" term.[8] Computationally, the significant thing to notice is that in the direct coulomb term the entire 2-space integral multiplies the function f for which we are trying to obtain a solution, whereas, in the exchange term, f is <u>inside</u> the 2-space integral. The exchange operator is thus a non-local operator, i.e., the exchange operator in the equation for $f(1)$ is <u>different</u> from the exchange operator in the equation for $g(1)$.

III. DERIVATION OF PRINCIPAL EQUATIONS

A. Outline of the Derivation of the Fock Equations

We desire the minimum of

$$E = \langle \Psi|H|\Psi \rangle / \langle \Psi|\Psi \rangle \tag{3}$$

---

[8] In the case of N electrons f would be replaced by u_i, g by u_j and each term would be summed over all j including j = i. The exchange term would include only those u_j for which the spin is the same as the u_i spin. This last distinction did not arise in our simple example as we took both electrons to have the same spin.

where $\Psi(\vec{x}_1, \vec{x}_2, \ldots \vec{x}_N) = \det[\phi_i(\vec{x}_j)]$; $\vec{x}_j$ contains both space and spin coordinates.

$$H = \sum_{i=1}^{N} (-\hbar^2/2m)\nabla_i^2 + \sum_{i=1}^{N} U(\vec{r}_i) + 1/2 \sum_{i=1}^{N}\sum_{j=1}^{N} e^2/|\vec{r}_1 - \vec{r}_2| \qquad (4)$$

The three terms in H are, respectively, kinetic, nuclear, and electron-electron interaction.

It would thus appear that the evaluation of eq. (3) is a formidable task: there are N kinetic energy operators, N nuclear operators, and $N(N-1)/2$ electron-electron operators; the determinant of $[\phi_i(\vec{x}_j)]$ appearing on the left and right of H has N! terms, each term containing N $\phi(\vec{x})$ factors. Orthogonality relations and recognition of dummy variables make the task tractable.

The orthogonality conditions are

$$\int \phi_k^*(\vec{x}_\ell)\phi_m(\vec{x}_\ell)d\tau_\ell = \delta_{km} . \qquad (5)$$

The denominator of eq. (3) then becomes simply N!. The first two terms in H contain only one-variable operators; in App. A we show that they give:

$$(-\hbar^2/2m) \sum_{j=1}^{N} \int \phi_j^*(\vec{r}_1)\nabla_1^2\phi_j(\vec{r}_1)d\tau_1 \qquad (A)$$

and

$$\sum_{j=1}^{N} \int \phi_j^*(\vec{r}_1)U(\vec{r}_1)\phi_j(\vec{r}_1)d\tau_1 \qquad (B)$$

respectively; $\vec{r}$ contains space coordinates only. The third term in H acts on two coordinates; in App. B we show that this gives:

$$\frac{1}{2} e^2 \sum_{k=1}^{N} \sum_{\ell=1}^{N} {}' \{ \int \frac{|\phi_k(\vec{r}_1)|^2 \ |\phi_\ell(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2$$

$$- \delta \text{ (spin 1, spin 2) } \int \frac{\phi_k{}^*(\vec{r}_1)\phi_\ell{}^*(\vec{r}_2)\phi_k(\vec{r}_2)\phi_\ell(\vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2 \}$$

<div align="right">(C)</div>

The first integral in (C) is called the "direct" term; the second is called the "exchange" term.

We now want

$$\delta E = 0 \tag{6}$$

$$\delta E = \frac{\partial E}{\partial \phi_1{}^*} \delta\phi_1{}^* + \frac{\partial E}{\partial \phi_2{}^*} \delta\phi_2{}^* + \ldots + \frac{\partial E}{\partial \phi_N{}^*} \delta\phi_N{}^* + \text{(complex conjugate)} \tag{7}$$

These functions cannot all be varied independently since we want any variation to preserve the orthogonality conditions (eq. (5)). Using the method of Lagrange undetermined multipliers (effectively making each $\delta\phi_i{}^*$ independent) we can consider a particular $\delta\phi_i{}^*$ as an arbitrary variation; $\delta E = 0$ then leads to the requirement that $(\frac{\partial E}{\partial \phi_i{}^*}) = 0$. This gives

$$- (\hbar^2/2m)\nabla_1{}^2\phi_i(\vec{r}_1) + U(\vec{r}_1)\phi_i(\vec{r}_1) + \sum_j \lambda_{ij}\phi_j(\vec{r}_1)$$

$$+ e^2 \{ [\sum_{j=1}^{N} {}' \int \frac{|\phi_j(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\tau_2]\phi_i(\vec{r}_1)$$

$$- \sum_{j=1}^{N} {}' \delta(\text{spin i, spin j}) \ [\int \frac{\phi_j{}^*(\bar{r}_2)\phi_i(\bar{r}_2)}{|\bar{r}_1 - \bar{r}_2|} d\tau_2]\phi_j(\bar{r}_1) \} = 0 \tag{8}$$

(There is a similar equation for each ϕ_i.) We note that there is considerable confusion in the literature as to whether one can diagonalize the λ_{ij} in the non-closed-shell case (see App. C); we shall assume that we cannot and proceed to derive the BM equation (their eq. (I)) on that basis.

B. Derivation of Eq. (I) of BM from the Fock Equations

As far as the labelling of core-electrons is concerned the BM model treats metallic NH_4 as if it were "funny sodium"; thus the 11 electrons are taken to be in a $1s^2 2s^2 2p^6 3s$ configuration. The 10-electron ion problem is first solved separately (including exchange terms). The resulting 1s, 2s, 2p "core" functions are then taken as fixed and an equation like eq. (8) is written for the 3s (valence) electron.

Since we are writing an equation for $\phi_i \equiv \psi_{3s}$, i.e., for a function with $\ell = 0$, there is no need to include the 2p term in $\sum \lambda_{ij}$; this term is automatically orthogonal to ψ_{3s} due to having a different ℓ value. We also take $\lambda_{ii} = - \varepsilon_{3s}$. We substitute

$$\phi_j(\vec{r}_1) = (\tilde{u}_j(r_1)/r_1)Y_{\ell j}(\theta_1,\phi_1) \tag{9}$$

where $Y_{\ell j}$ is a spherical harmonic (a similar substitution is made for $\psi_{3s}(\vec{r}_1)$) and write $\tilde{V}_o(r_1)$ for $U(\vec{r}_1)$, with

$$\tilde{V}_o(r_1) = - 7/r_1 - 4/r_o \qquad r_1 \leq r_o$$
$$= - 11/r_1 \qquad r_1 \geq r_o$$

as per BM. The tilde signifies that these functions are not yet in atomic units. As shown in App. D we obtain:

$$- \frac{\hbar^2}{2m} \frac{d^2 \tilde{u}(r_1)}{dr_1^2} + \tilde{V}_o(r_1) \tilde{u}(r_1) + \frac{e^2 \tilde{Z}_{eff}(r_1)}{r_1} \tilde{u}(r_1)$$

$$- e^2 \sum_j^{1s,2s,2p} \delta(\text{spins}) [\int \frac{\tilde{u}_j(r_2) \tilde{u}(r_2)}{|\vec{r}_1 - \vec{r}_2|} Y_{\ell j}^*(\theta_2, \phi_2) dr_2 d(\cos\theta_2) d\phi_2]$$

$$\times \tilde{u}_j(r_1) Y_{\ell j}(\theta_1, \phi_1) = \epsilon_{3s} \tilde{u}(r_1) - \tilde{\lambda}_{1s} \tilde{u}_{1s}(r_1) - \tilde{\lambda}_{2s} \tilde{u}_{2s}(r_1) . \quad (10)$$

It is legitimate to let the $\sum_j$ above run only over 1s, 2s, 2p (no 3s): originally this sum included ψ_{3s} but for metallic NH_4 there is only one ψ_{3s} function (just one electron in outer shell); thus the ψ_{3s} term in the direct coulomb terms is exactly cancelled by the ψ_{3s} term in the exchange terms.

We next put this equation into atomic units (see App. E).

$$- \frac{d^2 u(r)}{dr^2} + V_o(r) u(r) + \frac{2Z_{eff}(r)}{r} u(r)$$

$$- 2 \sum_j^{1s,2s,2p} \delta(\text{spins}) [\int \frac{u_j(r_1) u(r_1)}{|\vec{r}_1 - \vec{r}|} Y_{\ell j}^*(\theta_1, \phi_1) dr_1 d(\cos\theta_1) d\phi_1]$$

$$\times u_j(r) Y_{\ell j}(\theta, \phi) = \epsilon_{3s} u(r) - \lambda_{1s} u_{1s}(r) - \lambda_{2s} u_{2s}(r) . \quad (11)$$

V_o, Z_{eff}, ϵ_{3s}, and the λ's are now in Rydbergs.

The final step is to manipulate the exchange term to obtain a purely radial equation. This is done in App. F. A key point here is that we are dealing with closed ℓ subshells; this makes $\sum_j Y_{\ell j}^*(\theta_1, \phi_1) \times Y_{\ell j}(\theta, \phi)$ invariant under rotations, i.e., dependent only on the angle between $\vec{r}$ and $\vec{r}_1$. We obtain:

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$$[-d^2/dr^2 + V(r) - \epsilon_{3s}]u(r) + \lambda_{1s}u_{1s}(r) + \lambda_{2s}u_{2s}(r) =$$

$$2 \sum_{n\ell}^{1s,2s,2p} \{r^{-\ell-1}\int_0^r u_{n\ell}(r_1)u(r_1)r_1^{\ell}dr_1 + r^{\ell}\int_r^a u_{n\ell}(r_1)u(r_1)r_1^{-\ell-1}dr_1\}u_{n\ell}(r)$$

$$(12)$$

with

$$V(r) \equiv V_o(r) + 2Z_{eff}(r)/r$$

and

$$V_o(r) = -14/r - 8/r_0 \qquad r \leq r_0$$

$$= -22/r \qquad\qquad r \geq r_0$$

in atomic units. Eq. (12) is eq. (I) of BM. We have also obtained the identical final form following Fock.[9]

There are two (apparently both typographic) errors in BM's eq. (I):

(1) $r^{-\ell-1}$ in their last integral should be $r_1^{-\ell-1}$.

(2) the $(2\ell + 1)$ factor in their $\sum_{n\ell}$ should be[10] 1.

The factor 2 multiplying V and ϵ in BM's eq. (I) is due to their expressing these entities in Hartrees (1 Hartree = 2 Rydberg).

---

[9] V. Fock, Z. f. Phys. **81**, 195 (1933).

[10] A number of other references have eq. (12) as we've written it (without the $(2\ell + 1)$ factor in the exchange term). This would appear to be a typographic error in the BM paper: For an a value of 3.68 a.u., BM get a ground state E (including exchange) $\approx$ -7.5 ev. We obtain -6.90 ev. using the correct expression and -9.65 ev. using the $(2\ell + 1)$ factor. The much smaller discrepancy between our (correct factor) value and their value indicates that they probably used the correct factor in their actual computation.

IV. RESULTS - OUR CALCULATION <u>IGNORING</u> EXCHANGE

In this section we describe our (unsuccessful) attempts to reproduce BM's curve I: ground-state energy vs "a" (the Wigner-Seitz radius) with exchange ignored.

A. Calculation with the Lagrange Multipliers λ_{1s} and λ_{2s} Set Equal to Zero

Without exchange and with λ_{1s} and λ_{2s} set (arbitrarily) to zero, eq. (I) of BM is:

$$[-d^2/dr^2 + V(r)]u(r) = \varepsilon u(r) , \qquad (13)$$

with boundary conditions:

$$u(0) = 0 \qquad (14a)$$

$$du(r)/dr\big|_a = 0 \qquad (14b)$$

The computer program "WAVEB" is used to solve eq. (13). This program, based on the Numerov technique, is outlined in App. G. Results[11] for the two values of "a" used are shown in Table 1.

TABLE 1. GROUND-STATE ENERGIES WITHOUT EXCHANGE

$$\lambda_{1s} = \lambda_{2s} = 0$$

a (a.u.)	ε(ev.) This calc.	ε(ev.) BM
3.68	2.74	-1.26
4.80	-2.11	-4.37

---

[11] All BM energy values listed in this report are estimated from their Figure 1.

Our $\Delta\epsilon$ between the two "a" values is 4.85 ev, not even close to the BM value of 3.11 ev. (see their Figure 1, curve I).

B. "Expectation" Value

Our next step was to orthogonalize the $u(r)$ determined in section A to $u_{1s}(r)$ and $u_{2s}(r)$ using a Schmidt procedure and to then find the "expectation" value:

$$\epsilon \quad \equiv \quad \left\langle u^{\perp}(r) \left| -d^2/dr^2 + V(r) \right| u^{\perp}(r) \right\rangle \tag{15}$$

The computer program "DSPLSW", based on a spline routine[12], is used to evaluate the numerical derivative involved here[13]. The computer program "EINL" evaluates eq. (15). Three comments on these programs are in order:

(1) An attempt to avoid taking _any_ derivative through expansion of $u^{\perp}(r)$ in terms of u, u_{1s}, and u_{2s} would involve considerable algebra plus values for ϵ_{1s} and ϵ_{2s}.

(2) In using DSPLSW, $du^{\perp}(r)/dr|_0$ is found graphically.

(3) The $u_{2s}(r)$, written as $P_{2s}(r)$ in BM's notation, is not orthogonal to their $u_{1s}(r)$. It is straightforward but tedious to show that one obtains the same $u^{\perp}(r)$ whether or not one first orthogonalizes u_{2s} to u_{1s}.

---

[12]We are indebted to Ray Scanlon for furnishing this program and for discussions related to its use.

[13]Integration by parts allows us to write

$$\int_0^a u^{\perp}(d^2u^{\perp}/dr^2)dr = u^{\perp}(du^{\perp}/dr)\Big|_0^a - \int_0^a (du^{\perp}/dr)^2 dr \ .$$

The boundary conditions $u^{\perp}(0) = 0$, $(du^{\perp}/dr)\big|_a = 0$, make the first term vanish; thus, only the first derivative of $u^{\perp}$ is needed.

Results for the same two "a" values employed in Section A, above, are shown in Table 2.

TABLE 2. $\langle \epsilon \rangle$ WITHOUT EXCHANGE

(See Eq. (15) of the Text)

a (a.u.)	$\langle \epsilon \rangle$ (ev.) This Calc.
3.68	1.11
4.80	-2.71

Our $\Delta\epsilon$ between the two "a" values is approximately 3.8 ev, again not very close to BM's $\Delta\epsilon$ of 3.1 ev.

C. No-Exchange Calculation Including λ_{1s} and λ_{2s}

From the failure of the two previous approaches to reproduce the BM no-exchange-term curve, it appeared one should include λ_{1s} and λ_{2s} and use a "3-dimensional" search technique (for λ_{1s}, λ_{2s}, and ϵ); i.e., we are now solving:

$$[-d^2/dr^2 + V(r)]u(r) = \epsilon u(r) - \lambda_{1s}u_{1s}(r) - \lambda_{2s}u_{2s}(r) \qquad (16)$$

with conditions

$$\langle u|u_{1s} \rangle = \langle u|u_{2s} \rangle = 0 \qquad (17)$$

in addition to the boundary conditions expressed by eqs. (14a) and (14b). We use the computer program "TWAVE". The bulk of the 3-dimensional search logic is contained in a subroutine utilizing a "Rosenbrock" technique.[14] A narrative description of the TWAVE program is given in App. H.

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[14]The Rosenbrock-search subroutine used here was written by Ray Scanlon.

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Results for the two values of "a" previously used are shown in Table 3.

TABLE 3.   NO-EXCHANGE CASE

a (a.u.)	ϵ (ev.) Our 3-d Calc.
3.68	1.62
4.80	-2.63

Our $\Delta\epsilon$ is 4.25 ev., not very near BM's $\Delta\epsilon$ of 3.11 ev. At this time we have no explanation as to why our $\Delta\epsilon$ as calculated here differs so much from that of BM.

For completeness, and since the $u(r)$ of eq. (16) is needed as starting input for the iterative solution including exchange (discussed in the next section) we've calculated ϵ without exchange for a number of values of "a." These results and those of BM are listed in columns three and four, respectively, of Table 4; our no-exchange results are also compared with those of BM in the upper part of Figure 1.

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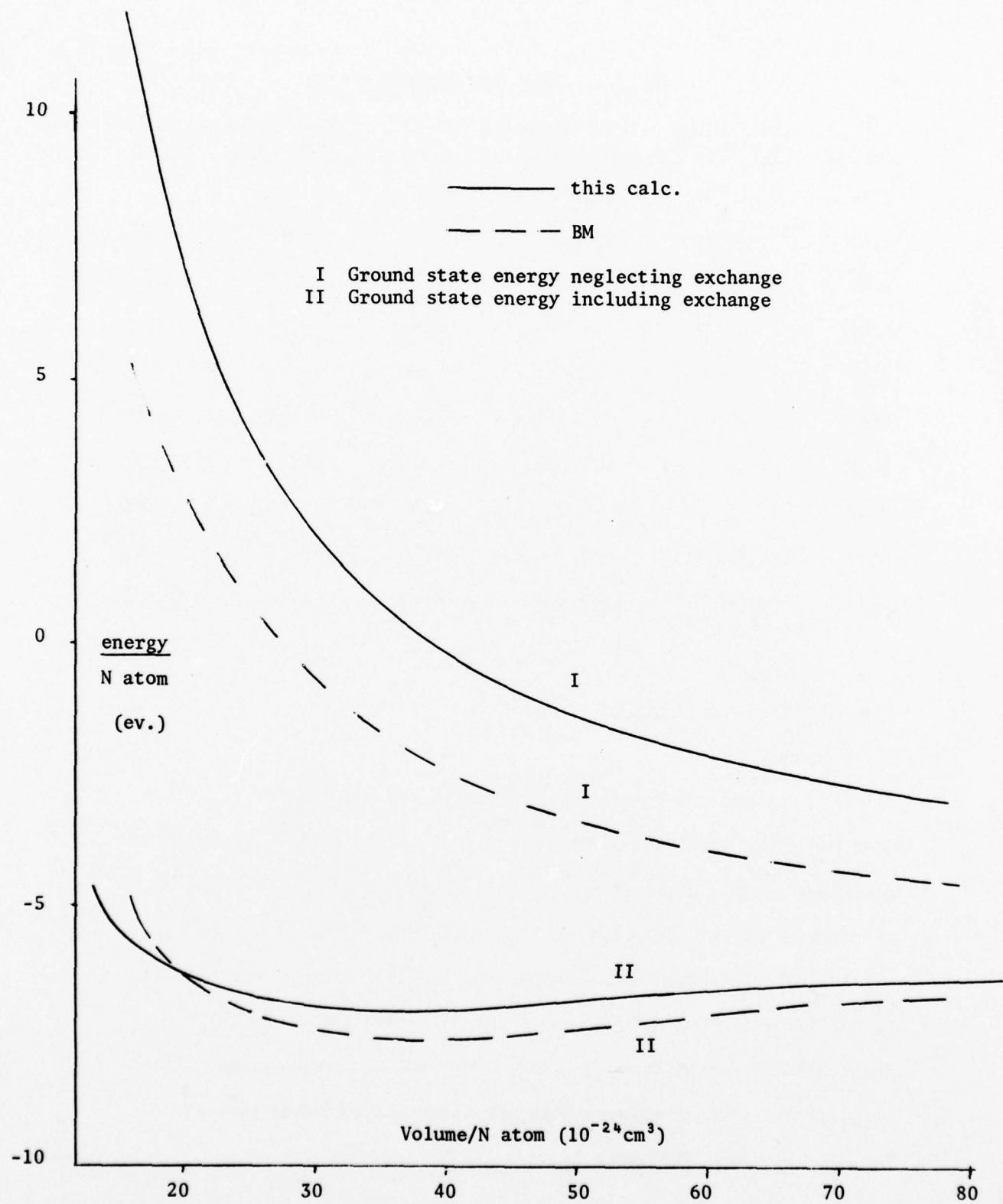
Figure 1. Calculated energy-volume relations at 0°K for metallic ammonium.

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TABLE 4. AMMONIUM RESULTS

a (a.u.)	Vol/N atom (10^{-24}cm^3)	No exchange (ev.) This calc.	BM	With Exchange (ev.) This calc.	BM
2.24	6.98	38.82	>10.	2.610	>3.
2.56	10.41	22.23	>7.	-3.226	~1.0
2.88	14.83	12.60	>5.	-5.573	-4.20
3.36	23.55	4.670	0.95	-6.721	-7.05
3.68	30.93	1.619	-1.26	-6.898	-7.52
4.00	39.72	- .337	-2.63	-6.886	-7.60
4.48	55.81	-1.830	-3.95	-6.717	-7.32
4.80	68.64	-2.627	-4.37	-6.584	-6.95
5.12	83.31	-3.136	-4.70	-6.431	-6.65
5.44	100.0	-3.468	-4.75	-6.282	-6.35

V. OUR CALCULATION INCLUDING EXCHANGE

A. Procedure

In this section we are concerned with the solution of eq. (12) with the right-hand side included; $u(r)$ must also satisfy the boundary conditions expressed by eqs. (14a) and (14b). We follow the procedure as outlined by BM. To start the iterative process we first use the solution obtained ignoring exchange for $u_{(0)}(r)$, namely, the solution to eq. (16) obtained using TWAVE. The $u(r)$ obtained using TWAVE is first orthogonalized to $u_{1s}(r)$ and $u_{2s}(r)$ and then normalized. This $u^{\perp}_{(0)}(r)$ function is then used to calculate the exchange term $g(r)$. We then solve eq. (12) with $\lambda_{1s} = \lambda_{2s} = 0$.

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$$[-d^2/dr^2 + V(r) - \epsilon]u_{(k+1)}(r) = -g_{(k)}(r) \qquad (18)$$

with

$$g_{(k)}(r) = -\sum_{n\ell}^{1s,2s,2p} 2 \{r^{-\ell-1}\int_0^r u_{n\ell}(x)u^{\perp}{}_{(k)}(x)x^{\ell}dx$$

$$+ r^{\ell}\int_r^a u_{n\ell}(x)u^{\perp}{}_{(k)}(x)x^{-\ell-1}dx\}u_{n\ell}(r) \qquad (19)$$

The $u(r)$ found by solving eq. (18) is then orthogonalized to $u_{1s}(r)$ and $u_{2s}(r)$ and then renormalized. This $u^{\perp}{}_{(k)}(r)$ is substituted into eq. (19) and the resulting $g_{(k)}(r)$ is used as input to eq. (18) to obtain $u_{(k+1)}(r)$. This process is continued until "convergence" is obtained. We have used four cycles in most cases; convergence appears to be obtained in three cycles. Convergence here is in the sense that the orthogonalized and normalized $u^{\perp}{}_{(k+1)}(r) \approx u^{\perp}{}_{(k)}(r)$ and the unorthogonalized $u_{(k+1)}(r) \approx u_{(k)}(r)$. The (unorthogonalized) $u(r)$ solution of eq. (18) does <u>not</u> appear to be converging to $u^{\perp}(r)$, i.e., orthogonalization remains significant no matter how large k becomes.[15]

The operations above are performed in the computer program "COMBINE": orthogonalization and renormalization are done in sub-routine RENOM using a Schmidt procedure; $g(r)$ as given in Eq. (19) is evaluated in subroutine XCHNG; eq. (18) is solved in MAIN of COMBINE using a Numerov technique similar to that of WAVEB (see App. G).

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[15]It is not at all clear that this procedure of solving eq. (12) with $\lambda_{1s} = \lambda_{2s} = 0$ and then orthogonalzing the resultant $u(r)$ to u_{1s} and u_{2s} is valid; we comment on this at some length in App. I.

B. Results (Including Exchange)

Columns five and six of Table 4 give our results and those of BM for various values of "a" for the exchanged-included case; these results are also compared in the lower part of Figure 1. Our values are roughly 0.5 ev. above BM's over most of the important part of the volume range (20 to 60 on the horizontal scale of Figure 1).

BM calculated total energy by adding the mean Fermi energy ε_F to the ground-state energy including exchange. The mean Fermi energy was calculated on a free-electron basis following Mott.[16] Since our ground-state curve is some 0.5 ev. higher than BM's and since our ε_F is identical to theirs, our total (internal) energy U will also be some 0.5 ev. above theirs. Our values for U are compared with those of BM in Table 5.

To obtain the difference in energy between metallic NH_4 and the $NH_3 - \frac{1}{2} H_2$ mixture we follow BM (see their eq. (3)).

$$[NH_4, \text{ metal}] = [NH_3, \text{ gas}] - A_p + (\varepsilon + \varepsilon_F)_o \qquad (20a)$$

where A_p is the proton affinity of NH_3.

$$[NH_3, \text{ crystal}] + \frac{1}{2} [H_2, \text{ crystal}] = [NH_3, \text{ gas}] - I_H - \frac{1}{2} D(H_2) - B$$
$$(20b)$$

where I_H is the ionization energy of atomic hydrogen, $D(H_2)$ is the dissociation energy of H_2 and

$$B = \text{B.E.}(NH_3, \text{ crystal}) + \frac{1}{2} \text{B.E.}(H_2, \text{ crystal}) , \qquad (20c)$$

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[16]N.F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys," Oxford (1936). (Dover (1958), pp. 54,55).

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TABLE 5.   AMMONIUM RESULTS

U vs V

Vol/N atom (10^{-24} cm^3)	ϵ_F (ev)	Total energy, U (ev) This calc	BM
6.98	5.963	8.573	>4.
10.41	4.565	1.339	>2.
14.83	3.607	-1.966	-0.59
23.55	2.650	-4.071	-4.40
30.93	2.209	-4.689	-5.31
39.72	1.870	-5.016	-5.73
55.81	1.491	-5.226	-5.83
68.64	1.299	-5.285	-5.65
83.31	1.141	-5.290	-5.51
100.0	1.011	-5.271	-5.45

$\epsilon_F = (3/5)E_{max}$

$\quad = (3/5)(3/\pi)^{2/3}(\pi^2\hbar^2/2m)(N/\Omega)^{2/3}$, using eq. (19), Chap II, ref. 16.

N/Ω = (# of electrons)/(unit volume) = $3/4\pi a^3$

$\epsilon_F = (3/10)(9\pi/4)^{2/3}(\hbar^2/ma^2)$, the expression used by BM.

Then, $\epsilon_F = (1.10)(27.2)/a^2 = (29.92)/a^2$

U = Ground state energy (including exchange) + ϵ_F

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[16]N. F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys," Oxford (1936). (Dover (1958), pp. 54,55).

the sum of the respective binding energies. The desired mixture
energy is then

$$[\text{mixture}] = [NH_3, \text{ gas}] - I_H - \frac{1}{2} D(H_2) - B - \varepsilon_{12} \qquad (20d)$$

where the positive quantity ε_{12} is the reduction in energy (per NH_3
molecule) due to mixing the two molecular crystals (our notation
differs somewhat from BM's). The various entities in eqs. (20a) -
(20d) are depicted in Figure 2; this picture is consistent with eq.
(3) of Stevenson[1] (Stevenson's B includes our ε_{12}).

Following BM, we take the various binding energies (B and ε_{12})
as being negligible. Eqs. (20a) and (20d) then give:

$$[NH_4, \text{ metal}] - [\text{mixture}] = (\varepsilon + \varepsilon_F)_o - A_p + I_H + D/2 \qquad (21)$$

BM obtained a minimum U for the metal some 0.86 ev. above the minimum
for the mixture; we obtain ~ 1.4 ev. for this difference. Our total[17]
(internal) energy curve is compared with BM's in Figure 3. (Stevenson's
metallic and mixture curves are also shown.) The zero of energy for
Figure 3 is that of infinitely dispersed NH_4^+ ions and electrons:

$$U(\text{zero pressure})_{\text{mixture}} = A_p - I_H - D/2 - B - \varepsilon_{12} . \qquad (22)$$

This is consistent with BM's Figure 1 and with Stevenson's Figure 1.
(As above, the B and ε_{12} terms may be neglected.) Stevenson obtains
the mixture curve from

$$U(P) = U(0) - \int_o^P P'(dV(P')/dP')dP' . \qquad (23)$$

[1]D. J. Stevenson, Nature 258, 222 (1975).
[17]Ground-state energy (with exchange) plus ε_F.
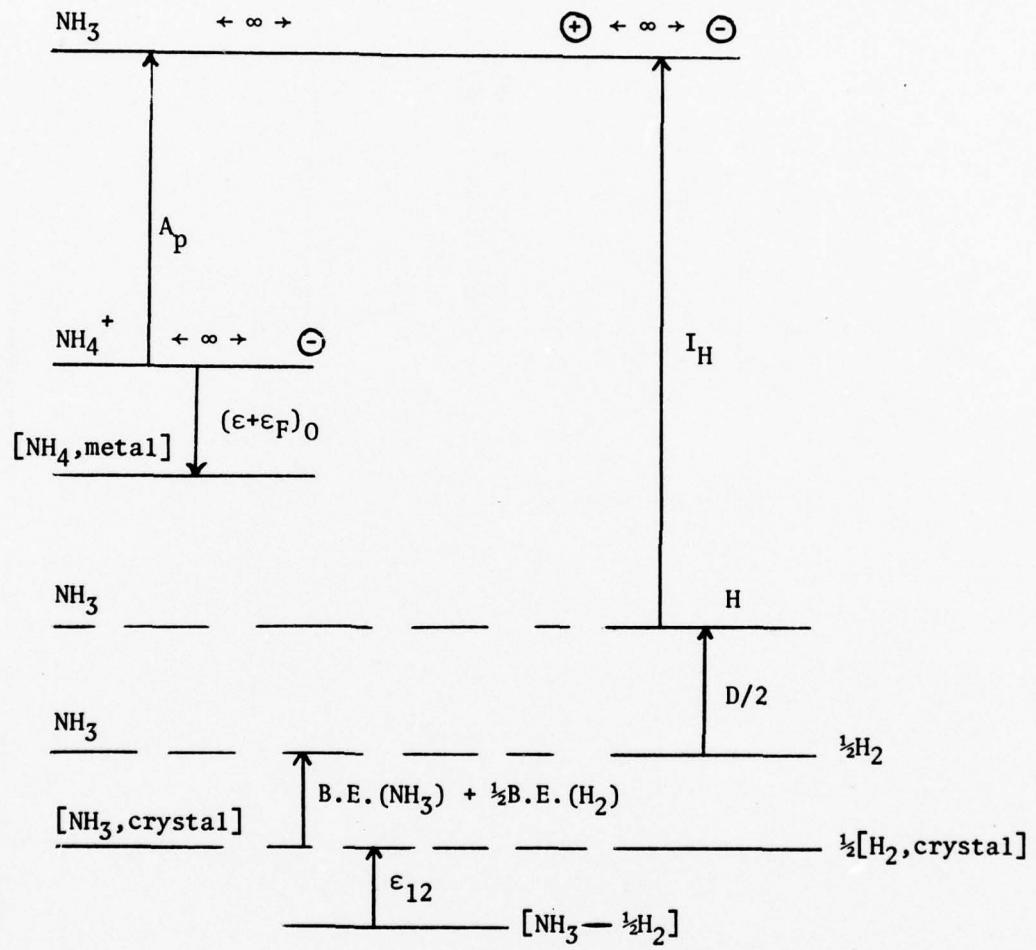
Figure 2. Schematic energy picture.
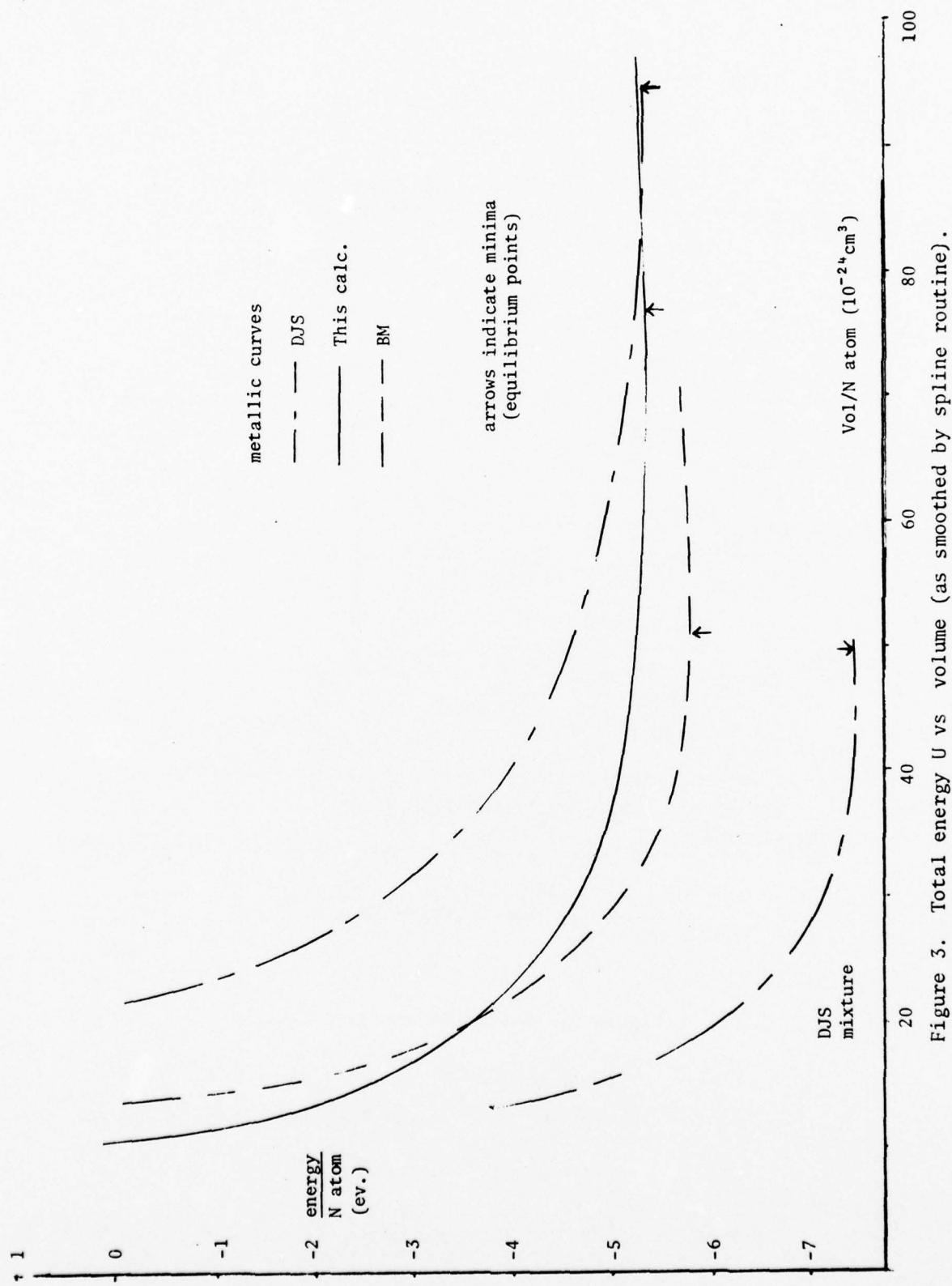
Figure 3. Total energy U vs volume (as smoothed by spline routine).

$$V(P) = V(NH_3,P) + \frac{1}{2} V(H_2,P) \tag{24}$$

where $V(NH_3,P)$ and $V(H_2,P)$ are the molecular volume-pressure relations of ammonia and hydrogen solids, respectively. Stevenson obtained $V(NH_3,P)$ by interpolating between the experimental[18] equation of state at low pressure (P < 20 kbar) and the theoretical equation of state at high pressure (P $\gtrsim$ 2 Mbar) calculated[19] from Thomas-Fermi-Dirac theory. $V(H_2,P)$ is taken from Ross's analysis[20] of the Livermore shock data.

There are three differences between our metallic NH_4 U vs V curve and BM's curve:

1. Our equilibrium point is shifted considerably toward Stevenson's value of ~ 95 x 10^{-24} cm^3/N atom (5.35 a.u. radius). We obtain ~ 76.7 (4.99 a.u.) whereas BM obtained[21] 47 (4.23 a.u.). At small volume (high pressure) our curve tends to agree with BM's; at very large volume (low pressure) our curve approaches Stevenson's.

2. At the respective equilibrium volumes our internal energy is about 0.5 ev. higher than BM's. BM obtained -5.84 ev.; we obtain -5.35 ev. (Stevenson has -5.36 ev.). The 0.5 ev difference between our curve and BM's exists over a sizable part of the volume range.

[18]J. W. Stewart, J. Chem. Phys. 33, 128 (1956).

[19]E. E. Salpeter and H. S. Zapolsky, Phys. Rev. 158, 876 (1967).

[20]M. Ross, J. Chem. Phys. 60, 3634 (1974).

[21]Given in their text; their Figure 1 indicates approximately 52 (4.38 a.u.)

3. Over a considerable part of the range of interest our curve has a smaller slope leading to smaller pressure at a given volume.

We agree with Stevenson (Ref. 1) that BM's transition pressure (P_t) estimate is invalid due to their <u>not</u> obtaining an $NH_3 - \frac{1}{2} H_2$ equation of state. BM, using only the mixture equilibrium <u>point</u>, estimate P_t to be 100 kbar with a range from 60 to 140 kbar based on an 0.5 ev. uncertainty in A_p[22].

In computing the Gibbs energy ($G = U + PV - TS$; T taken as zero), the differences (#2 and #3 as listed above) between our U vs V and BM's tend to cancel and we obtain essentially the same $G(P)$ curve as they do. At <u>very</u> low pressure our curve tends to approach Stevenson's (see Figure 4).

VI. SUMMARY AND CONCLUSIONS

This technical report is primarily concerned with the BM calculation for metallic NH_4. Our calculation, being essentially a repeat of BM's, suffers from the same deficiencies, namely:

1. The calculation is essentially atomic. (Probably minor.)

2. Sphericized NH_4^+ ion. (Probably minor.)

3. Rigid r_0 (radius of hydrogen "shell").

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[1] D. J. Stevenson, Nature <u>258</u>, 222 (1975).

[22] Our total energy curve (U vs V) for the metal would lead to $P_t \sim 135$ kbar using the BM procedure; we emphasize again that this procedure is invalid.

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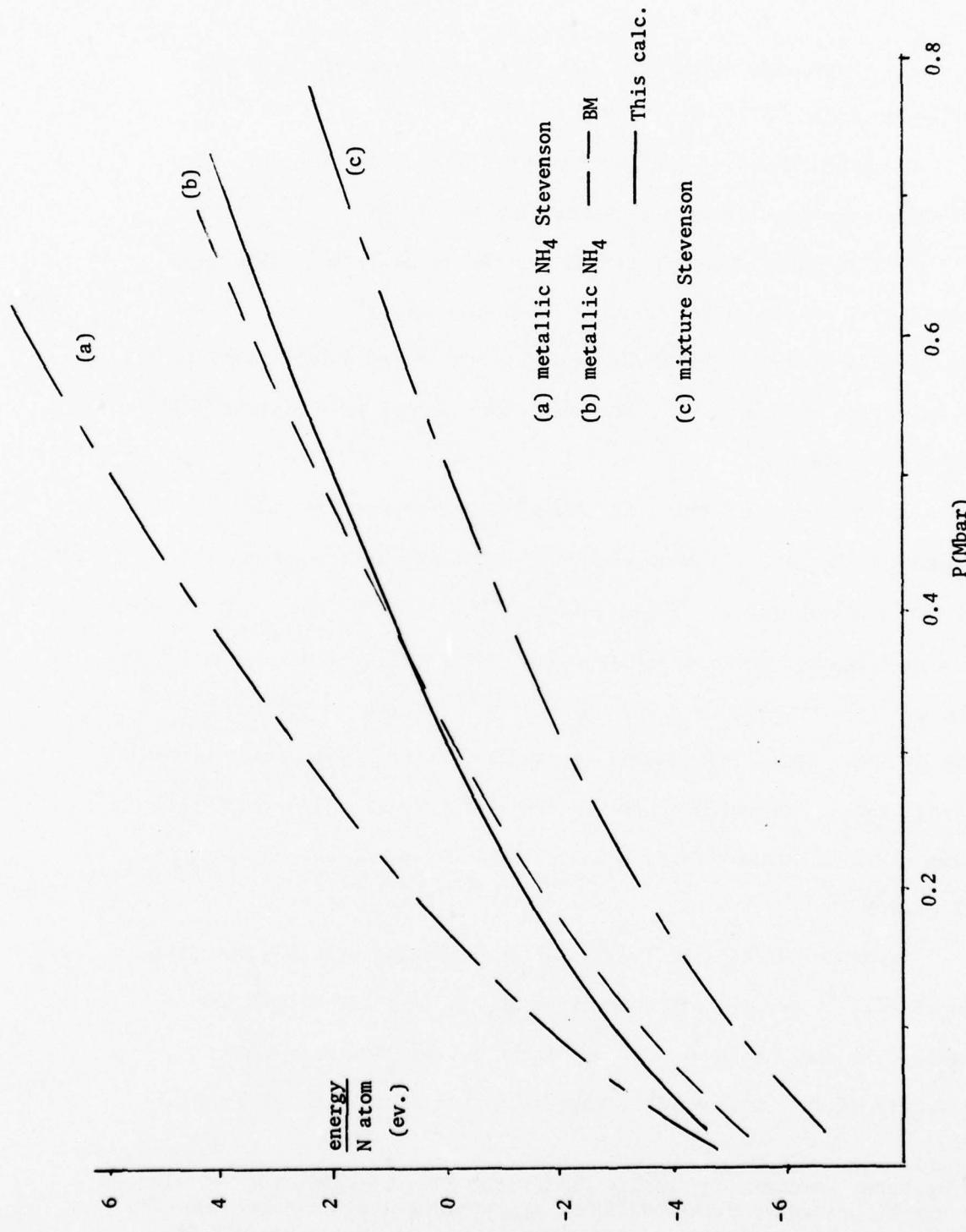
Figure 4. Gibbs energy vs pressure at 0°K.

(a) metallic NH_4 Stevenson

(b) metallic NH_4 — — BM

——— This calc.

(c) mixture Stevenson

P(Mbar)

$\dfrac{energy}{N\ atom}$ (ev.)

4. Rigid core states (1s, 2s, 2p), merely renormalized for different values of "a".

5. Approximation made in using BM's iterative procedure for solving their eq. (I) with exchange (our eq. (12)).

6. Free electron calculation for the Fermi level. (Probably significant, particularly at the higher pressures.)

The major deficiency in the BM paper is associated with their attempt to calculate the transition pressure; they do <u>not</u> have a curve for the $NH_3 - \frac{1}{2} H_2$ mixture!

As outlined in Section IV, our attempts to duplicate BM's curve I (ground-state metallic energy without exchange) were unsuccessful. Our attempts included: Simply solving BM's eq. (I) (our eq. (12)) with exchange ignored and with $\lambda_{1s} = \lambda_{2s} = 0$ (Sec. IV.A.); orthogonalizing the resultant $u(r)$ to u_{1s} and u_{2s} and then finding an "expectation" energy (Sec. IV.B.); including λ_{1s} and λ_{2s} using a Rosenbrock technique (Sec. IV.C.). Comparison between the latter calculation and BM's is summarized in columns three and four of Table 4 and in the upper part of Figure 1.

Attempts to match BM's calculation including exchange were more successful[23]; results are summarized in the last two columns of Table 4 and in the lower part of Figure 1. We emphasize that the validity of BM's mathematical approach (solving our eq. (12) with

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[23]We have, however, not really duplicated BM's results; the differences may be primarily a reflection of the approximately two decades of development in electronic computers which took place between the two calculations.

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$\lambda_{1s} = \lambda_{2s} = 0$ and then orthogonalizing in combination with an iterative process) has not really been established.

Total internal energy U is given by the sum of ground-state energy (with exchange) and mean Fermi energy. Our U(V) curves as well as BM's and Stevenson's are shown in Figure 3. We find the internal energy at the equilibrium volume to be about 0.5 ev higher than that obtained by BM, i.e., ours is very close to Stevenson's value of -5.36 ev. We note that Stevenson uses a proton affinity value some 0.46 ev smaller than BM's'; this would tend to make Stevenson's U(V) curve correspondingly higher than BM's. We used the BM proton affinity value. Stevenson's equilibrium radius (for the metal) is 5.35 a.u.; BM's is 4.23 a.u. We obtain 4.99 a.u., i.e., shifted outward considerably toward Stevenson's value. The approximately 0.5 ev difference between our metallic U(V) and BM's exists over a sizable part of the volume range. Our U(V) has a smaller slope than BM's over a sizable part of the volume range; this leads to smaller pressure at a given volume.

In computing the Gibbs energy the last two differences tend to cancel and we obtain essentially the same G(P) curve as BM. At very low pressure our curve tends to approach Stevenson's (see Figure 4).

Stevenson[1,4] seems to feel fairly strongly that the desired transition will not take place and has suggested[4] that BM may have

[1]D. J. Stevenson, Nature 258, 222 (1975).

[4]D. J. Stevenson (private communication) (Letter to Curtis Selph, Oct. 1976).

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made a computational error. Our repeat of the BM calculation indicates
one <u>cannot</u> explain the difference between Stevenson's NH_4 curve and
BM's (see Figure 4) solely by computational error on the part of BM.[24]
As an argument in support of his results over BM's, Stevenson cites[4]
the fact that his equilibrium volume is much larger than BM's; our
calculation shows that, within the BM approach, one can shift the
equilibrium volume considerably <u>without</u> making an appreciable change
in $G(P)$. It is extremely difficult to estimate "error bars" for the
curves in Figure 4 (or Figure 3); they may be as large as 1-3 ev. In
our opinion, while a transition from the NH_3-$\frac{1}{2}H_2$ mixture to metallic
NH_4 in the funny sodium form is possible, it appears unlikely, par-
ticularly below about one Mbar.*

[4]D. J. Stevenson (private communication) (Letter to Curtis Selph,
Oct. 1976).

[24]This assumes that the BM 1s, 2s, and 2p wave functions are essentially
correct; we did not recalculate these. We note that Stevenson did
his calculation twice; once with the BM cores, once with another set -
the difference in equilibrium U was only 0.04 ev.; difference in
equilibrium radius only 0.17 a.u. Thus, recalculating the core wave
functions is unlikely to change our results.

*Note added in proof: Discussion with Dr. Stevenson indicates that
funny sodium is just <u>not</u> a good candidate for the metallic form of
NH_4 (assuming his mixture curve to be reasonably good, the volume
would have to change drastically to get a common U vs V tangent). It
is more probable to go to an arrangement such as H's forming an "fcc"
lattice with N sitting in the "body-center" position or possibly to a
metallic state formed by the overlapping in $\vec{k}$-space of the molecular
energy bands. Stevenson estimates the required pressures to be in the
Mbar (and above) range. After discussion of our results (see, in par-
ticular, the last paragraph of this report) Stevenson indicated that
BM may have an error in their physics (e.g., use of the free-electron
ϵ_F can lead to significant error).

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*The omitted numbers are footnotes.

28. L. Schiff, "Quantum Mechanics," McGraw-Hill (1949).

29. D. R. Hartree, "The Calculation of Atomic Structures," Wiley (1957), Chapter 4.

30. Ray Scanlon, private communication.

APPENDIX A

DERIVATION OF THE ONE-VARIABLE-OPERATOR
INTEGRALS OF THE HARTREE-FOCK EQUATION

Explicitly, the N-electron wave function Ψ of the main text is

$$\begin{vmatrix} \tilde{\phi}_1(\vec{x}_1) & \tilde{\phi}_1(\vec{x}_2) & \cdots & \tilde{\phi}_1(\vec{x}_N) \\ \tilde{\phi}_2(\vec{x}_1) & \tilde{\phi}_2(\vec{x}_2) & \cdots & \tilde{\phi}_2(\vec{x}_N) \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \tilde{\phi}_N(\vec{x}_1) & \tilde{\phi}_N(\vec{x}_2) & \cdots & \tilde{\phi}_N(\vec{x}_N) \end{vmatrix} \qquad (A-1)$$

with $\tilde{\phi}_i(\vec{x}_j) \equiv \phi_i(\vec{r}_j)s_i(\vec{\sigma}_j)$. $\phi_i(\vec{r}_j)$ is a purely spatial function. $s_i(\vec{\sigma}_j)$ can be either $\alpha(\vec{\sigma}_j)$ or $\beta(\vec{\sigma}_j)$ where

$$\alpha(\vec{\sigma}_j) = 1, \text{ if the spin-coordinate } \vec{\sigma}_j \text{ is up.}$$
$$= 0, \text{ if } \vec{\sigma}_j \text{ is down.}$$

$$\beta(\vec{\sigma}_j) = 0, \text{ if } \vec{\sigma}_j \text{ is up.}$$
$$= 1, \text{ if } \vec{\sigma}_j \text{ is down.}$$

The orthogonality condition (eq. (5) of the main text) written explicitly for space and spin is

$$\int \phi_k^*(\vec{r}_\ell)\phi_m(\vec{r}_\ell)d\tau_\ell \sum_{\sigma_\ell} s_k(\vec{\sigma}_\ell)s_m(\vec{\sigma}_\ell) = \delta_{km}\delta_{s_k,s_m} \qquad (A-2)$$

δ_{km} is a condition to be imposed on the spatial functions; δ_{s_k,s_m} is insured by the α,β definitions given above.

Consider $H_{kinetic}$ of eq. (4) of the main text; this one-variable operator acts on det $[\phi_i(\vec{r}_j)]$. (Since we deal here with a one-variable operator, and since the operator does not affect the spin, we can ignore the spin coordinate; in Appendix B, where we deal with a two-variable operator, we explicitly include the spin functions.) Now consider just one term of $H_{kinetic}$, namely ∇_1^2: ignoring the purely multiplicative factor this operator, acting on det $[\phi_i(\vec{r}_j)]$ gives

$$\sum_{j=1}^{N} \nabla_1^2 \phi_j(\vec{r}_1)[\text{permutations of } \phi_a(\vec{r}_b)]_j \qquad (A-3)$$

For each value of j the square bracket contains $(N-1)!$ terms, each with $(N-1)$ factors: $a = 1,2,\cdots,N$ ($a \neq j$); $b = 2,3,\cdots,N$. Combining this with $\text{det}^*[\phi_\ell(\vec{r}_k)]$ and using the orthogonality conditions we see that only one of the $N!$ terms of det^* "matches" (gives a non-zero integral) any particular term of (A-3), i.e.,

$$\phi_j^*(\vec{r}_1)[\text{correct permutation of } \phi_a^*(\vec{r}_b)]_j$$

matches

$$\nabla_1^2 \phi_j(\vec{r}_1)[\text{particular permutation of } \phi_a(\vec{r}_b)]_j \ .$$

This leads (for ∇_1^2 alone) to

$$(N-1)! \sum_{j=1}^{N} \int \phi_j^*(\vec{r}_1) \nabla_1^2 \phi_j(\vec{r}_1) d\tau_1 \ . \qquad (A-4)$$

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We obtain similar expressions for ∇_2^2, ∇_3^2, $\cdots$, ∇_N^2. Since the variable acted on in (A-4) is the variable of integration, each of ∇_1^2, ∇_2^2, etc., will give the same result. Thus (dividing by the N! of the denominator):

$$\langle \Psi | H_{kinetic} | \Psi \rangle / \langle \Psi | \Psi \rangle = -(\hbar^2/2m) \sum_{j=1}^{N} \int \phi_j^*(\vec{r}_1) \nabla_1^2 \phi_j(\vec{r}_1) d\tau_1 \quad (A-5)$$

This is (A) of the main text.

A similar treatment of $H_{nuclear}$ gives (B) of the main text.

APPENDIX B

DERIVATION OF THE TWO-VARIABLE-OPERATOR
INTEGRALS OF THE HARTREE-FOCK EQUATION

The third term of eq. (4) of the main text, the electron-electron interaction H_{el-el}, is a two-variable operator. Consider just one term of this operator, namely $1/|\vec{r}_1-\vec{r}_2|$, operating on det $[\tilde{\phi}_i(\vec{x}_j)]$. This gives

$$\sum_{k=1}^{N} \sum_{\ell=1}^{N} \frac{\phi_k(\vec{r}_1)\phi_\ell(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} s_k(\vec{\sigma}_1)s_\ell(\vec{\sigma}_2)[\text{Permutations of } \phi_a(\vec{r}_b)s_a(\vec{\sigma}_b)]_{k\ell}$$

(B-1)

For each choice of k,ℓ in the double sum, the square bracket contains $(N-2)!$ terms, <u>each</u> with $(N-2)$ factors: $a = 1,2,3,\cdots,N$ ($a \neq k,\ell$); $b = 3,4,\cdots,N$. when we multiply by $\text{det}^*[\tilde{\phi}_i(\vec{x}_j)]$, <u>two</u> of the N! terms in det^* will "match" any particular term of (B-1), i.e.,

$$\phi_k^*(\vec{r}_1)\phi_\ell^*(\vec{r}_2)s_k(\vec{\sigma}_1)s_\ell(\vec{\sigma}_2)[\text{correct permutation of } \phi_a^*(\vec{r}_b)s_a(\vec{\sigma}_b)]_{k\ell}$$

and

$$\phi_\ell^*(\vec{r}_1)\phi_k^*(\vec{r}_2)s_\ell(\vec{\sigma}_1)s_k(\vec{\sigma}_2)[\text{correct permutation of } \phi_a^*(\vec{r}_b)s_a(\vec{\sigma}_b)]_{k\ell}$$

match

$$\frac{\phi_k(\vec{r}_1)\phi_\ell(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} s_k(\vec{\sigma}_1)s_\ell(\vec{\sigma}_2)[\text{particular permutation of } \phi_a(\vec{r}_b)s_a(\vec{\sigma}_b)]_{k\ell}$$

as far as <u>spatial</u> functions are concerned. For the spin functions: s_k, s_ℓ can be any α,β combination for the first of the two matching terms; in the second matching term s_ℓ must equal s_k in order to have a non-zero value; this is readily seen to imply that, for this term, electrons 1 and 2 must have parallel spins. Thus, $1/|\vec{r}_1-\vec{r}_2|$ gives

$$(N-2)! \sum_{k\ell} \{ \int \frac{|\phi_k(\vec{r}_1)|^2 |\phi_\ell(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2$$

$$(B-2)$$

$$- \delta(\text{spins}) \int \frac{\phi_\ell^*(\vec{r}_1) \phi_k^*(\vec{r}_2) \phi_k(\vec{r}_1) \phi_\ell(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2 \}.$$

So far, we've considered only $1/|\vec{r}_1 - \vec{r}_2|$; there will be a total of $N(N-1)$ operators:

$$1/|\vec{r}_1 - \vec{r}_2|, \ 1/|\vec{r}_1 - \vec{r}_3|, \cdots, \ 1/|\vec{r}_1 - \vec{r}_N|, \ 1/|\vec{r}_2 - \vec{r}_1|, \cdots, \ 1/|\vec{r}_N - \vec{r}_{N-1}|.$$

$\vec{r}_i$, $\vec{r}_j$ in each $1/|\vec{r}_i - \vec{r}_j|$ are also the variables of integration in that particular case; thus, each operator gives the same result. Then (dividing by the N! of the denominator and replacing the $e^2/2$ multiplicative factor) we obtain (C) of the main text. (We've interchanged $\vec{r}_1$, $\vec{r}_2$ in the second integral of (B-2); this is clearly allowable due to the form of the operator.)

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APPENDIX C

CAN THE λ MATRIX APPEARING IN THE
FOCK EQUATIONS ALWAYS BE DIAGONALIZED?

There is considerable confusion on this point in the literature.
Reitz[25] states that one can <u>always</u> choose solutions such that λ is a
diagonal matrix (emphasis added). Reitz is dealing explicitly with the
crystal case. Slater, in his derivation of the Fock equations for the
atomic case[26], appears to show that a unitary transformation of the
one-electron functions $\phi_j(\vec{q_i})$ can be made which will diagonalize λ
(Section 17-1); however, in Section 17-5 (for non-closed shells) of
ref. 26 Slater states that one <u>cannot</u> diagonalize λ. In the crystal
case[27] Slater seems to indicate, in Section 1-2, that one <u>can</u> diagonalize
λ.

Without pursuing the matter further it would appear that the
crucial factor is whether one uses a <u>single</u> determinantal function
(λ diagonalizable) or whether one needs more than one determinantal
function (λ not, in general, diagonalizable).

[25] J. R. Reitz in "Solid State Physics," ed. Seitz and Turnbull, Vol. 1,
p. 1, Academic Press (1955).

[26] J. C. Slater, "Quantum Theory of Atomic Structure," Vol. 2, McGraw-
Hill (1960).

[27] J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 4,
McGraw-Hill (1974).

APPENDIX D

DERIVATION OF THE BERNAL-MASSEY EQUATION:

FIRST STEPS IN OBTAINING THE RADIAL EQUATION

In spherical coordinates

$$\nabla_r^2 = (1/r^2)\partial/\partial r(r^2\partial/\partial r) + (1/r^2)[(1/\sin\theta)$$

$$\times \partial/\partial\theta(\sin\theta\partial/\partial\theta) + (1/\sin^2\theta)\partial^2/\partial\phi^2] \qquad (D-1)$$

We know[28] that the square bracket of (D-1) operating on $Y_{\ell m}$ gives $-\ell(\ell+1)Y_{\ell m}$. Since $\ell = 0$ here, we may drop this term.

Eq. (8) of the main text then becomes

$$- \frac{\hbar^2}{2m} \frac{Y_0}{r_1} \frac{d^2\tilde{u}(r_1)}{dr_1^2} + \tilde{V}_o(r_1) \frac{Y_0}{r_1} \tilde{u}(r_1) + e^2 \frac{\tilde{Z}_{eff}(r_1)}{r_1^2} \tilde{u}(r_1)Y_0$$

$$-e^2 \sum_j^{1s,2s,2p} \delta(spins)[\int \frac{\phi_j^*(r_2)\tilde{u}(r_2)Y_0(\theta_2,\phi_2)}{|\vec{r}_1-\vec{r}_2|r_2} d\tau_2]\tilde{\phi}_j(r_1) \qquad (D-2)$$

$$= \varepsilon_{3s} \frac{\tilde{u}(r_1)}{r_1} Y_0 - \tilde{\lambda}_{1s} \frac{\tilde{u}_{1s}(r_1)}{r_1} Y_0 - \tilde{\lambda}_{2s} \frac{\tilde{u}_{2s}(r_1)}{r_1} Y_0$$

Since the Y_0 terms have no angular dependence and as all are normalized with the same factor $1/\sqrt{4\pi}$, we may simply factor out the Y_0; factoring out $1/r_1$ as well and substituting for ϕ_j as per eq. (9) of the main text, we obtain eq. (10) of the main text. The direct coulomb term has been replaced by an averaged term $\tilde{Z}_{eff}(r_1)/r_1$.

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[28] L. Schiff, "Quantum Mechanics," McGraw-Hill (1949). See eqs. (14.21) and (14.22), Chap. IV.

APPENDIX E

DERIVATION OF THE BERNAL-MASSEY EQUATION:

TRANSFORMING TO ATOMIC UNITS

Let

$$r = a_o\rho$$

with

$$a_o = \hbar/me^2 = 1 \text{ Bohr radius}$$

$$\hbar^2/2ma_o{}^2 = 1 \text{ Rydberg}$$

Also let

$$V_o(\rho_1) = \tilde{V}_o(r_1)$$

$$u(\rho) = \tilde{u}(r)$$

$$Z_{eff}(\rho_1) = \tilde{Z}_{eff}(r_1)$$

After all these substitutions have been made and the entire equation
multiplied by $2ma_o{}^2/\hbar^2$, replace ρ_1 and ρ_2 with r and r_1 respectively.
This gives eq. (11) of the main text.

APPENDIX F

DERIVATION OF THE BERNAL-MASSEY EQUATION:

MANIPULATION OF THE EXCHANGE TERM FOR CLOSED ℓ-SUBSHELLS

Due to the rotational invariance in eq. (11) of the main text we can always (in the integration over r_1) choose the polar axis to be in the r direction.
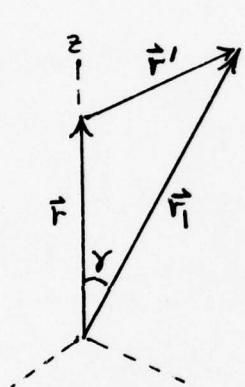
$$r^\prime = (r^2 + r_1^2 - 2rr_1 \cos\gamma)^{1/2}. \quad \text{(F-1)}$$

For $r_1 < r$,

$$r^\prime = r[1 + (r_1/r)^2 - 2(r_1/r)\cos\gamma]^{1/2}$$

$$= rX,$$

with $X^{-1} = \sum_{\ell^\prime=0}^{\infty} P_{\ell^\prime}(\cos\gamma)(r_1/r)^{\ell^\prime}.$

$$\text{(ref. 28, eq. (14.10))} \quad \text{(F-2)}$$

Similarly, for $r_1 > r$,

$$\frac{1}{r^\prime} = \frac{1}{r_1}\sum_{\ell^\prime=0}^{\infty} P_{\ell^\prime}(\cos\gamma)(r/r_1)^{\ell^\prime}. \quad \text{(F-3)}$$

For j standing for 1s, the $r_1 < r$ part of the exchange integral in eq. (11) of the main text is then

$$[\frac{1}{r}\int_{r_1=0}^{r} u_{1s}(r_1)u(r_1)\sum_{\ell^\prime=0}^{\infty}(r_1/r)^{\ell^\prime}dr_1 \int_{\gamma=0}^{\pi} P_{\ell^\prime}(\cos\gamma)d(\cos\gamma)\frac{1}{\sqrt{4\pi}}\int_{\phi_1=0}^{2\pi}d\phi_1] \quad \text{(F-4)}$$

using $Y_{1s} = 1/\sqrt{4\pi}$. Inserting $P_0(\cos\gamma) = 1$ into (F-4) and using (ref. 28, eq. (14.15)),

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[28] L. Schiff, "Quantum Mechanics," McGraw-Hill (1949).

$$\int_{\gamma=0}^{\pi} P_\ell(\cos\gamma)P_{\ell'}(\cos\gamma)d(\cos\gamma) = (2/[2\ell+1])\delta_{\ell\ell'} , \qquad (F\text{-}5)$$

the 1s exchange term (for $r_1 < r$) in eq. (11) becomes

$$-(2/r)[\int_{r_1=0}^{r} u_{1s}(r_1)u(r_1)dr_1]u_{1s}(r) . \qquad (F\text{-}6)$$

For $r_1 > r$ we have

$$-2[\int_{r_1=r}^{a} u_{1s}(r_1)u(r_1)(1/r_1)dr_1]u_{1s}(r) . \qquad (F\text{-}7)$$

There will be similar expressions for the 2s term.

For j standing for 2p

$$\sum_{m=-\ell}^{\ell} Y_{1m}^*(\theta_1,\phi_1)Y_{1m}(\theta,\phi) = (3/4\pi) \cos\theta_1 \cos\theta$$

$$+ (3/8\pi)\sin\theta_1 \sin\theta[e^{i(\phi-\phi_1)} + e^{-i(\phi-\phi_1)}]$$

$$= (3/4\pi)[\cos\theta_1 \cos\theta + \sin\theta_1 \sin\theta \cos(\phi-\phi_1)]$$

$$= (3/4\pi)\cos\gamma = (3/4\pi)P_1(\cos\gamma) . \qquad (F\text{-}8)$$

The 2p integral in eq. (11) is then (for $r_1 < r$) ,

$$[1/r \int_{r_1=0}^{r} u_{2p}(r_1)u(r_1) \sum_{\ell'=0}^{\infty} (r_1/r)^{\ell'} dr_1 \int_{\gamma=0}^{\pi} (3/4\pi)P_1(\cos\gamma)$$

$$\times P_{\ell'}(\cos\gamma)d(\cos\gamma) \int_{\phi_r=0}^{2\pi} d\phi_r] .$$

Using (F-5), the 2p exchange term (for $r_1 < r$) becomes

$$(-2/r^2)[\int_{r_1=0}^{r} u_{2p}(r_1)u(r_1)r_1 dr_1]u_{2p}(r) , \qquad (F\text{-}9)$$

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and (for $r_1 > r$),

$$-2r\left[\int_{r_1=r}^{a} \frac{u_{2p}(r_1)u(r_1)}{r_1^2}\, dr_1\right]u_{2p}(r) \ . \qquad \text{(F-10)}$$

Collecting eqs. (F-6) through (F-10), the entire exchange term can be written

$$-2\sum_{1s,2s,2p}\left\{r^{-\ell-1}\int_{o}^{r} u_{n\ell}(r_1)u(r_1)r_1^{\ell}dr_1\right.$$

$$\left. + r^{\ell}\int_{r}^{a} u_{n\ell}(r_1)u(r_1)r_1^{-\ell-1}dr_1\right\}u_{n\ell}(r) \ . \qquad \text{(F-11)}$$

Inserting this into eq. (11) of the main text and rearranging somewhat we obtain eq. (12) of the main text.

APPENDIX G

THE NUMEROV TECHNIQUE AND COMPUTER PROGRAM "WAVEB"

I. Basis of the Numerov Process and a Narrative Description of "WAVEB"

We note that "MAIN" of the computer program "COMBINE" is very similar to "WAVEB"; the differences are discussed in Part IV of this Appendix.

The treatment here is based on that of Hartree[29]. The Numerov process is applicable to linear second-order differential equations. Consider the equation

$$u'' = f(r)u + g(r) \qquad (G-1)$$

We treat three cases:

(1) No exchange; $\lambda_{1s} = \lambda_{2s} = 0$. Eq. (13) of main text.

(2) No exchange; λ's included.   Eq. (16) of main text.

(3) With exchange; $\lambda_{1s} = \lambda_{2s} = 0$. Eq. (18) of main text.

In all three cases:

$$f(r) \equiv V(r) - \varepsilon .$$

For case (1), $g(r) = 0$ $\qquad (G-1a)$

For case (2), $g(r) = \lambda_{1s}u_{1s}(r) + \lambda_{2s}u_{2s}(r)$ $\qquad (G-1b)$

For case (3), $g(r) = \sum_{1s,2s,2p} (-2)\{r^{-\ell-1}\int_{o}^{r}u_{n\ell}(x)u_{(k)}(x)x^{\ell}dx$

$$+ r^{\ell}\int_{r}^{a}u_{n\ell}(x)u_{(k)}(x)x^{-\ell-1}dx\}u_{n\ell}(r) \qquad (G-1c)$$

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[29] D. R. Hartree, "The Calculation of Atomic Structures," Wiley (1957), Chapter 4.

where $u_{(k)}(x)$ is the u of the previous go-round when we are solving eq. (G-1) for $u_{(k+1)}(r)$.

Define the "first difference" as

$$\delta u_{j+\frac{1}{2}} \equiv u_{j+1} - u_j \qquad (G-2)$$

where u_j is a shorthand notation for $u(r_j)$ where r_j here represents the value of r at the jth point of the r mesh. Define the "second difference" as

$$\delta^2 u_j \equiv \delta u_{j+\frac{1}{2}} - \delta u_{j-\frac{1}{2}} = u_{j+1} - 2u_j + u_{j-1} \qquad (G-3)$$

A Taylor series expansion of u leads to

$$\delta^2 u_j = (\Delta r)^2 [u_j'' + \frac{1}{12} \delta^2 u_j'' - \frac{1}{240} \delta^4 u_j''] + O(\Delta r)^8 . \qquad (G-4)$$

We will ignore the δ^4 term and the $O(\Delta r)^8$ term in eq. (G-4). Combining eqs. (G-1), (G-3), and (G-4) gives

$$u_{j+1} = \frac{1}{(S-f_{j+1})} \{u_j[2S+10f_j] - u_{j-1}[S-f_{j-1}] + g_{j+1} + 10g_j + g_{j-1}\} \qquad (G-5)$$

with $S \equiv 12/(\Delta r)^2$

An inspection of eq. (G-5) shows that u_{j+1} depends on the u values of the two "previous" (further left) points j and j-1. Thus, some other procedure must be used to determine u_j near r = 0. This "starting" procedure is based on the expansion

$$u_{n\ell}(r) = Ar^{\ell+1}(1 + \alpha r + \beta r^2 + \gamma r^3 + \cdots) \qquad (G-6)$$

near r = 0. Substitution of (G-6) into (G-1) and solution in series allows evaluation of α, β, and γ in terms of f and g. This is used to generate u(2) and u(3). (From (G-6), u(0) = 0.0.) The explicit evaluation of α, β, γ is given in Part II of this appendix.

WAVEB may be thought of as a two-part process: the first involves getting the correct number of nodes; the second involves getting zero slope at the $r = a$ end of the mesh. Both parts involve a number of iterations (typically on the order of 30 altogether).

Part one of WAVEB proceeds by an iterative process as follows: An initial guess is made for ε (read in as input data). $u(2)$ and $u(3)$ are then found using eq. (G-6). The remaining $u(r)$ are then generated (for $j = 4$ to $j = N$) using eq. (G-5). An atomic-like function labeled by quantum numbers n and ℓ must have $n-\ell-1$ nodes. Once $u(r)$ for $j = 1,N$ is generated, the number of nodes are counted and ε is changed to $\varepsilon+\Delta\varepsilon$ or to $\varepsilon-\Delta\varepsilon$ to start the next iteration. From the form of eq. (G-1) and either eq. (13) or (16) of the main text one sees that ε should be made more positive if there are too few nodes (need more curvature) etc. The magnitude of the initial $\Delta\varepsilon$ step is read in as data; as subsequent iterations "zero-in" to just produce the right number of nodes within the prescribed mesh, the size of $\Delta\varepsilon$ is reduced.

When the correct number of nodes are found (with the last node sufficiently close to the $r = a$ point) the program switches to part two - the slope test. The form of eqs. (G-1) and (13) or (16) indicate that when

$$(\text{slope})(\text{sign of } u(N))$$

is negative (indicates slope is <u>toward</u> the horizontal axis; less curvature is required) one should decrease ε; when positive, one should increase ε. This process is continued until $|\Delta\varepsilon|$ becomes smaller than some preset value.

II. Evaluation of α, β, and γ for the "Starting" Procedure

For u_{3s}, eq. (G-6) is (for r near r = 0),

$$u_{(k+1)}(r) = A_{(k+1)}(r + \alpha r^2 + \beta r^3 + \gamma r^4) . \qquad (G-7)$$

From eq. (12) of the main text,

$$V(r) \equiv V_o(r) + 2Z_{eff}(r)/r$$

$$= -14/r - 8/r_o + 2Z_{eff}(r)/r, \quad (r \text{ near } r = 0).$$

For the three cases listed in connection with eq. (G-1)

$$f(r) = -14/r - 8/r_o + 2Z_{eff}(r)/r - \epsilon . \qquad (G-8)$$

Expanding $Z_{eff}(r)$ in a taylor series (for r near r = 0),

$$f(r) = -14/r + 2Z'_{eff}(0) - 8/r_o - \epsilon + rZ''_{eff}(0) \qquad (G-9)$$

where we have used $Z(0) = 0.0$. $Z'_{eff}(0)$ and $Z''_{eff}(0)$, as well as A_{ns} and $A_{ns}a_{ns}$ introduced later, may be evaluated by expanding the appropriate function ($Z_{eff}(r)$ or $u_{ns}(r)$) in a Taylor series for the first three non-zero values of the function and solving the resultant equations simultaneously. We use the $Z_{eff}(r)$ of BM's Table I. We obtain $Z'_{eff}(0) = 20.1340$ and $Z''_{eff}(0) = -17.4959$; $r_o = 1.84$ as per BM.

Substituting (G-7) and (G-9) into (G-1) we obtain

$$A_{(k+1)}[2\alpha + 6\beta r + 12\gamma r^2] - g(r)$$

$$+ [14/r + R_\epsilon - rZ''_{eff}(0)]A_{(k+1)}[r + \alpha r^2 + \beta r^3 + \gamma r^4] = 0 \qquad (G-10)$$

with

$$R_\epsilon \equiv \epsilon + 8/r_o - 2Z'_{eff}(0) \qquad (G-11)$$

Case (1): $g(r) = 0$

Equating coefficients of the various powers of r to zero separately (keeping terms to order r^2 only), we obtain

$$\alpha = -7$$

$$\beta = -[14\alpha + R_\epsilon]/6 \qquad\qquad (G-12)$$

$$\gamma = [Z_{eff}''(0) - 14\beta - \alpha R_\epsilon]/12$$

Cases (2) and (3)

From (G-6),

$$u_{1s}(r) = A_{1s}(r + a_{1s}r^2 + b_{1s}r^3 + c_{1s}r^4)$$

$$u_{2s}(r) = A_{2s}(r + a_{2s}r^2 + b_{2s}r^3 + c_{2s}r^4)$$

$$u_{2p}(r) = A_{2p}(r^2 + a_{2p}r^3 + b_{2p}r^4 + c_{2p}r^5) \ . \qquad (G-13)$$

To order r^2, $g(r)$ can be written

$$g(r) = A_{1s}M_{1s}(r + a_{1s}r^2) + A_{2s}M_{2s}(r + a_{2s}r^2) \ . \qquad (G-14)$$

For case (2), M_{ns} is clearly just λ_{ns}. In Part III of this appendix we show that $g(r)$ for case (3) can be written as in eq. (G-14) with

$$M_{ns} = -2\int_o^a u_{ns}(x)u_{(k)}(x)x^{-1}dx \ , \qquad\qquad (G-15)$$

for the $u_{(k+1)}$ solution. M_{ns} for case (3) is evaluated in Subroutine "AUX2" of "COMBINE". (We note that the u_{2p} function does not appear in $f(r)$ for r near r = 0.) When (G-14) is substituted into (G-10) and the resultant equation is reordered we obtain

$$A_{(k+1)}[2\alpha + 14] + \{A_{(k+1)}[14\alpha + 6\beta + R_\epsilon] - \sum_{n=1}^{2}(A_{ns}M_{ns})\}r \qquad (G-16)$$

$$+ \{A_{(k+1)}[\alpha R_\epsilon + 14\beta + 12\gamma - Z_{eff}''(0)] - \sum_{n=1}^{2}(A_{ns}M_{ns}a_{ns})\}r^2 = 0 \ .$$

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Equating coefficients of the various powers of r to zero separately (keeping terms to order r^2 only), we obtain

$$\alpha = -7$$

$$\beta = -[14\alpha + R_\epsilon - A_{(k+1)}^{-1} \sum_{n=1}^{2} (A_{ns}M_{ns})]/6 \qquad \text{(G-17)}$$

$$\gamma = [Z_{eff}''(0) - \alpha R_\epsilon - 14\beta + A_{(k+1)}^{-1} \sum_{n=1}^{2} (A_{ns}M_{ns}a_{ns})]/12 \ .$$

III. Evaluation of M_{ns} for Case (3).

Using eq. (G-7) for $u_{(k)}(x)$ and eq. (G-13) for $u_{n\ell}$, the first integral in eq. (G-1c) becomes

$$A_{n\ell}^2 A_{(k)}[1 + a_{n\ell}r + b_{n\ell}r^2 + \cdots]$$

$$\times \int_0^r x^{\ell+1}[1 + a_{n\ell}x + b_{n\ell}x^2 + \cdots]x[1 + \alpha x + \beta x^2 + \cdots]x^\ell dx \ .$$

(The $r^{-\ell-1}$ and $u_{n\ell}(r)$ factors of (G-1c) have been included in the expression above.) The lowest-power term is

$$A_{n\ell}^2 A_{(k)} \int_0^r x^{2\ell+2} dx = A_{n\ell}^2 A_{(k)} r^{2\ell+3}/(2\ell+3) \ . \qquad \text{(G-18)}$$

We are interested only in terms of $O(r^2)$ or lower (see eq. (G-16)). Thus, even for $\ell = 0$, this first integral term may be ignored.

We rewrite the second integral term in eq. (G-1c) as

$$r^\ell u_{n\ell}(r)[\int_0^a - \int_0^r] \qquad \text{(G-19)}$$

The first integral in (G-19) must be a constant (independent of r); writing $C_{n\ell}$ for this constant, this first term of (G-19) becomes

$$r^\ell A_{n\ell} r^{\ell+1}[1 + a_{n\ell}r + \cdots]C_{n\ell}$$

using eq. (G-13); we rearrange this as

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$$A_{n\ell}C_{n\ell}r^{2\ell+1}[1 + a_{n\ell}r + \cdots] \qquad \text{(G-20)}$$

For $u_{2p}(\ell=1)$, this will be $O(r^3)$ and higher: thus u_{2p} can be ignored here. For $\ell = 0$ we have

$$A_{ns}C_{ns}r + A_{ns}C_{ns}a_{ns}r^2 + \cdots \qquad \text{(G-21)}$$

which must be considered. Using eq. (G-7) for $u_{(k)}(x)$ and eq. (G-13) for $u_{n\ell}$, the second integral in (G-19) becomes

$$-A_{n\ell}^2 A_{(k)}r^{2\ell+1}[1 + a_{n\ell}r + \cdots]$$

$$\times \int_o^r x^{\ell+1}[1 + a_{n\ell}x + \cdots]x[1 + \alpha x + \cdots]x^{-\ell-1}dx \ .$$

(The $r^\ell u_{n\ell}(r)$ of eq. (G-1c) or (G-19) is included in this expression.) The lowest-power term is

$$-A_{n\ell}^2 A_{(k)}r^{2\ell+1}\int_o^r xdx = -A_{n\ell}^2 A_{(k)}r^{2\ell+3}/2 \qquad \text{(G-22)}$$

which is of $O(r^3)$ even for $\ell = 0$; thus, this term may be ignored.

Thus, contributions to the "starting" equation from $g(r)$ come only from u_{1s} and u_{2s} as indicated by (G-21); this gives, for r near $r = 0$,

$$g(r) = -2 \sum_{n=1}^2 A_{ns}[\int_o^a u_{ns}(x)u_{(k)}(x)x^{-1}dx](r + a_{ns}r^2) \qquad \text{(G-23)}$$

verifying eqs. (G-14) and (G-15) for case (3), i.e., for the exchange case with $\lambda_{1s} = \lambda_{2s} = 0$.

IV. Difference Between MAIN of "COMBINE" and "WAVEB"

The overall routing of "COMBINE" is shown in Figure 5. The
discussion in Parts I, II and III of this appendix applies to MAIN of
COMBINE as well as to WAVEB.

Our older system for generating an atomic-like wave function
worked reasonably well on a single-shot basis but isn't good for the BM
problem where we "recycle", i.e., where the whole iteration is repeated
again with a new $g(r)$. (In this discussion the word "iteration"
refers to a new guess at the energy ϵ for a given $g(r)$; the word
"cycle" refers to the set of ϵ iterations for a fixed $g(r)$.)

The specific problem with the older system is the result of several
factors. By the third or fourth cycle "convergence" is fairly well
obtained (input u $(r) \approx$ output u (r)). Under the old system, $u(r)$
is forced to have an <u>extra</u> node, then energy is decreased somewhat and
$\epsilon, u(r)$ are found which give zero slope. After, say, the third cycle,
the input energy for the first iteration of the fourth cycle is just
about right to give zero slope with the <u>correct</u> number of nodes;
however, the old system forces an increase in energy to create an
<u>extra</u> node, i.e., forces one <u>away</u> from the proper $u(r)$.

In the <u>new</u> system the program: (1) Gets the correct number of
nodes. (2) Increases the energy, pushing the last (greatest r value)
node inward until this last node is some preset number of spaces in
from the end of the mesh. (3) Juggles the energy to give zero slope
at $r = a$. Since the new system needs only 25 - 35 iterations/cycle,
we start each cycle with the original $|\Delta\epsilon|$. We have also put the

Preliminary
Read mesh, potential, etc.
Read $u_0(r)$ from "TWAVE"
Read $u_{1s}(r)$, $u_{2s}(r)$, $u_{2p}(r)$
Normalize u_{1s}, u_{2s}, u_{2p}
Obtain $\langle u_{1s} | u_{2s} \rangle$
Read initial ϵ, $|\Delta\epsilon|$

cycles
loop

AUX2   Evaluate M_{ns} of (G-15)

XCHNG   Evaluate $g(r)$ of (G-1c)

iterations
loop

Obtain $u(r)$
by Numerov process

Switching

Proper # of nodes?

no   yes

Room to fit slope?

no   yes

Apply slope test

$|\Delta\epsilon|$ small enough?

no   yes

change ϵ
appropriately

RENOM Orthogonalize u to u_{1s}, u_{2s}
Renormalize

Print ϵ, $u(r)$

Figure 5.   Block diagram for "COMBINE."

DE-DEMIN test (the test for proper exit from the ε-iteration loop) on both the positive $\Delta\varepsilon$ and negative $\Delta\varepsilon$ sides.

Results of these changes: the first real run of COMBINE using the old system involved five cycles; the fifth cycle required 292 iterations! With the new system this cycle obtained virtually the same final ε (differed by 1 in the 7th significant digit) using only 29 iterations. Secondly, using a starting $\Delta\varepsilon$ for this fifth cycle equal to (original $\Delta\varepsilon$)/10 only shortened the number of iterations by 6; the original $\Delta\varepsilon$ (equal to 0.1 Ry in this case) gave virtually the same final ε and final $\Delta\varepsilon$ and produced a small enough final slope; thus the new system just uses the same starting $\Delta\varepsilon$ (of order of 0.1 Ry) for every cycle.

APPENDIX H

THE "TWAVE" PROGRAM

I. A Narrative Description of "TWAVE"

The heart of the 3-dimensional search is in Subroutine DRSNIN, a
Ray Scanlon routine based on the Rosenbrock technique. Initial guesses
for λ_1, λ_2, and ε and the initial step sizes for each are read in as
data. The unnormalized BM $u_{1s}(r)$ and $u_{2s}(r)$ functions are read in and
normalized.

DRSNIN contains a sophisticated search procedure. For each
"dimension" the routine first steps in the positive direction, then in
the negative direction if necessary; a success (smaller "object"
function) followed by a failure (larger object function) terminates
the search in that direction. Step sizes are automatically adjusted.
Thus, DRSNIN attempts to minimize the object function which in our
case is

$$(\text{weight factor})[du(r)/dr|_a]^2 + \left\langle u|u_{1s}\right\rangle^2 + \left\langle u|u_{2s}\right\rangle^2$$

(H-1)

This reflects the boundary conditions: zero slope at r = a; u orthogonal
to u_{1s} and u_{2s}. The object function is evaluated in Function (Subroutine)
H(X). H(X) calls Subroutine LWAVE which uses the Numerov technique
(see App. G) to find u(r). When u(r) contains the _wrong_ number of
nodes a large number (10000.) is substituted for $du(r)/dr|_a$ in the
object function. The program can be run in either of two modes:
(1) Terminates after a preset number of cycles or when the object

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function becomes smaller than some preset value, which ever occurs first. (2) Terminates after a preset number of cycles. If mode (2) is used, one gets an indication of the convergence from a simple inspection of the print-out. It should be noted that, typically, the object function is evaluated many times within one "cycle".

II. Normalization of $u(r)$

Because of the presence of the $\lambda_{ns}u_{ns}(r)$ terms, eq. (16) of the main text is <u>not</u> a standard eigenvalue equation. Defining

$$\hat{0} \equiv -d^2/dr^2 + V(r) , \qquad (H-2)$$

$$g(r) \equiv \lambda_1^0 u_{1s}(r) + \lambda_2^0 u_{2s}(r) , \qquad (H-3)$$

we may write eq. (16) as

$$\hat{0}u(r) + g(r) = \varepsilon u(r) . \qquad (H-4)$$

Suppose eq. (H-4) has been solved to obtain ε, $u(r)$. Now define

$$U(r) \equiv u(r)/N \qquad (H-5)$$

with $N = \langle u|u \rangle^{1/2}$ so that $\langle U|U \rangle = 1$. Substituting (H-5) into (H-4) we obtain

$$\hat{0}U(r) + g(r)/N = \varepsilon U(r) . \qquad (H-6)$$

If we now define a new $G(r)$:

$$G(r) \equiv \lambda_1 u_{1s}(r) + \lambda_2 u_{2s}(r) \qquad (H-7)$$

with $\lambda_i = \lambda_i^0/N$, so that $G(r) = g(r)/N$,

$$\hat{0}U(r) + G(r) = \varepsilon U(r) \qquad (H-8)$$

showing that $U(r)$ satisfies essentially the same equation as $u(r)$, with the same ε, but with new values of λ_1 and λ_2.

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APPENDIX I

COMMENTS ON THE VALIDITY OF THE BERNAL-MASSEY
PROCEDURE FOR SOLUTION OF THEIR EQUATION (I)

Within the approximations of the BM model (i.e., solving the _ion_ problem first, _then_ adding $\psi_{3s}(r) \equiv u(r)$ while keeping the core functions fixed) the $u_{2s}(r)$ equation is

$$-u_{2s}''(r) + V_{2s}(r)u_{2s}(r) - \epsilon_{2s}u_{2s}(r)$$
$$+ \lambda_{1s,2s}u_{1s}(r) = -g_{2s}(r) \qquad (\text{I}-1)$$

where

$$V_{2s}(r) \equiv V_o(r) + 2Z_{eff}^{2s}(r)/r ,$$
$$Z_{eff}^{2s}(r) \equiv 2Z_{1s}(r) + Z_{2s}(r) + 6Z_{2p}(r) ,$$
$$g_{2s}(r) = g(u_{2s},u_{1s}) + g(u_{2s},u_{2p}) ,$$

with

$$g(u_{n'o},u_{n\ell}) \equiv -2\{r^{-\ell-1}\int_o^r u_{n\ell}(x)u_{n'o}(x)x^\ell dx$$
$$+ r^\ell \int_r^a u_{n\ell}(x)u_{n'o}(x)x^{-\ell-1}dx\}u_{n\ell}(r) ,$$

and $V_o(r)$ is the potential due to the nucleus plus the four hydrogen protons. Eq. (I) of BM (in our atomic units) is

$$-u''(r) + V_{3s}(r)u(r) - \epsilon_{3s}u(r) + \lambda_{3s,1s}u_{1s}(r)$$
$$+ \lambda_{3s,2s}u_{2s}(r) = -g_{3s}(r) , \qquad \text{(I) of BM}$$

with

$$V_{3s}(r) \equiv V_o(r) + 2Z_{eff}^{3s}(r)/r \ ,$$

$$Z_{eff}^{3s}(r) \equiv 2Z_{1s}(r) + 2Z_{2s}(r) + 6Z_{2p}(r) \ ,$$

$$g_{3s}(r) = g(u,u_{1s}) + g(u,u_{2s}) + g(u,u_{2p}) \ .$$

We note that

$$V_{3s}(r) - V_{2s}(r) = 2Z_{2s}(r)/r \ . \qquad (I-2)$$

In the BM iterative procedure for determining $u(r)$ and ε_{3s}, the "last go-round" equation looks like

$$[-d^2/dr^2 + V_{3s}(r) - \varepsilon_{3s}]u^u(r) = -g_{3s}^{\perp}(r) \qquad (I-3)$$

where $g_{3s}^{\perp}(r)$ uses $u^{\perp}(r)$ instead of $u^u(r)$. The superscript u means "unnormalized"; the superscript $\perp$ means "orthogonalized, normalized". Explicitly:

$$u^{\perp}(r) = [u^u(r) + \alpha u_{2s}(r)]/N \ , \qquad (I-4)$$

$$N = \left\langle u^u + \alpha u_{2s} | u^u + \alpha u_{2s} \right\rangle^{\frac{1}{2}} \ ,$$

$$\alpha = - \left\langle u^u | u_{2s} \right\rangle \ ,$$

The significant differences to note between BM's eq. (I) and our eq. (I-3) are that eq. (I-3) has the λ's set equal to zero and has an unorthogonalized and unnormalized "solution u" ($u^u(r)$) different from the $u^{\perp}(r)$ used in getting the exchange term $g_{3s}^{\perp}(r)$. (We've assumed "convergence", i.e., $u^{\perp}(r)$ of the jth cycle $\approx u^{\perp}(r)$ of the (j-1)th cycle.)

We adopt the point of view that: if $u^{\perp}(r)$ is a "proper solution" to the problem it should satisfy eq. (I) of BM; we first rewrite (I):

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$$[-d^2/dr^2 + V_{3s}(r)]u(r) = \varepsilon_{3s}u(r)$$

$$-\lambda_{3s,2s}u_{2s}(r) - g_{3s}(r) \ . \qquad (I-5)$$

(We've set $\lambda_{3s,1s} = 0$ as did BM; our numerical work also indicates $\left\langle u_{1s} | u^u \right\rangle$ is small.) We now put $u^{\perp}(r)$ into the left-hand-side (LHS) of eq. (I-5) and see if we can obtain the RHS:

$$\text{LHS of } (I-5) = [-d^2/dr^2 + V_{3s}(r)]u^{\perp}(r)$$

$$= (1/N)[-d^2u^u/dr^2 + V_{3s}u^u]$$

$$+ (\alpha/N)[-d^2u_{2s}/dr^2 + V_{3s}u_{2s}] \ ,$$

$$= (1/N)[\varepsilon_{3s}u^u - g_{3s}^{\perp}]$$

$$+ (\alpha/N)[(\varepsilon_{2s}+V_{3s}-V_{2s})u_{2s}-g_{2s}-\lambda_{1s,2s}u_{1s}] \ ,$$

using eqs. (I-1) and (I-3). With some manipulation we obtain

$$\text{LHS} = \varepsilon_{3s}u^{\perp} - (\alpha/N)[\varepsilon_{3s} - \varepsilon_{2s}]u_{2s} - g_{3s}^{\perp} \qquad (I-6)$$

$$+ (\alpha/N)[(V_{3s} - V_{2s})u_{2s} - g_{2s} - \lambda_{1s,2s}u_{1s}]-[(1-N)/N]g_{3s}^{\perp} \ .$$

This equals the RHS of (I-5) if:

1. $\lambda_{3s,2s} = (\alpha/N)[\varepsilon_{3s} - \varepsilon_{2s}]$

and

2. The second line of (I-6) $\rightarrow 0$.

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TABLE I-1. NUMERICAL EVALUATION OF "EXTRA" TERMS IN EQ. (I-6)

This evaluation is for a = 3.68.

$$\epsilon_{3s} = -0.507, \quad \alpha = 0.302, \quad N = 0.629$$

r	$\epsilon_{3s}u^{\perp}$	1st term on 2nd line of (I-6)	$[(N-1)/N]g_{3s}^{\perp}$	total 2nd line of (I-6)
0.4	.083	-.147	.030	-0.117
1.04	.245	-.250	.276	0.026
2.08	-.173	-.080	-.025	-0.105
3.04	-.389	-.019	-.034	-0.053
3.68	-.426	-.008	-.017	-0.025

Table I-1 gives an indication of the size of the "extra" terms relative to $\epsilon_{3s}u^{\perp}$ for some selected r values. We see from the table that the extra terms are small for $r \gtrsim 3.0$ but are not small in general; thus, it is not clear that the BM procedure is valid.

APPENDIX J

COMMENTS ON TRANSLATING U vs V TO G vs P

The important point is that getting the slope $(P = -dU/dV)$ from published curves of U vs V is difficult to do accurately. People who do this frequently, feel that, even with the typical 3" x 4" figure from a journal article, it is better to assign numerical x,y values from the figure and run them through a spline routine than to try to take the slope from the figure directly.[30]

TABLE J-1. DETERMINATION OF P,G FROM STEVENSON'S METALLIC U vs V PLOT (REF. 1)

Volume		P[a]	PV	U	G
(S units)	(BM units)	(Mbar)	(ev)	(ev)	(ev)
13.15	21.85	1.27	17.35	0.11	17.46
13.93	23.14	0.984	14.20	-0.73	13.47
15.0	24.92	0.659	10.25	-1.63	8.62
15.8	26.25	0.494	8.09	-2.10	5.99
16.7	27.70	0.384	6.66	-2.50	4.16
17.5	29.07	0.321	5.84	-2.80	3.04
20.0	33.22	0.192	3.98	-3.44	0.54
25.0	41.53	0.106	2.76	-4.15	-1.39
30.0	49.83	0.080	2.48	-4.65	-2.17
35.0	58.14	0.0406	1.48	-4.96	-3.48
40.0	66.44	0.0218	0.910	-5.104	-4.194
50.0	83.06	0.0144	0.745	-5.300	-4.555
57.1	94.85	0.0	0.0	-5.360	-5.360

[a]From DSPLSW 6/28/77

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[1]D. J. Stevenson, Nature 258, 222 (1975).

[30]Ray Scanlon, private communication.

The spline routine we use[12], DSPLSW, fits a cubic function over segments (preserving continuity). Our first attempts with DSPLSW led to non-monotonically decreasing (magnitude) slopes. A better choice of end points and end-point slopes seemed to improve matters.

TABLE J-2. DETERMINATION OF P,G FROM BM'S METALLIC

U vs V PLOT (REF. 2)

Volume (BM units)	P[a] (Mbar)	PV (ev)	U (ev)	G (ev)
13.8	1.65	14.20	0.28	14.48
15.0	1.35	12.65	-1.10	11.55
17.88	0.76	8.55	-2.96	5.59
18.95	0.60	7.10	-3.42	3.68
20.0	0.47	5.90	-3.76	2.14
23.52	0.24	3.54	-4.51	-0.97
26.85	0.167	2.69	-4.92	-2.23
30.0	0.121	2.27	-5.21	-2.94
35.0	0.067	1.45	-5.48	-4.03
40.0	0.048	1.20	-5.66	-4.46
49.0	0.014	0.430	-5.846	-5.42
55.0	-0.010[b]	-0.327	-5.850	
60.0	-0.018[b]	-0.684	-5.804	
70.0	-0.024[b]	-1.029	-5.670	

[a]From DSPLSW 6/22/77
[b]Computed pressure is negative

[2]M. J. M. Bernal and H. S. W. Massey, Mon. Not. R. Astr. Soc. 114, 172 (1954).
[12]We are indebted to Ray Scanlon for furnishing this program and for discussions related to its use.

Selected values of the pertinent entities are given in Tables J-1 through J-4 for Stevenson metallic, BM metallic, present metallic, and Stevenson (Ross) mixture, respectively. For the volume entries the Stevenson (S) units are $cm^3/mol\ NH^4$; the BM units are $(cm^3/N\ atom)$ x 10^{24}. The U values in Tables J-2 and J-3 differ somewhat from those in columns three and four of Table 5 due to smoothing of the U vs V curves by the DSPLSW routine; this is more noticeable at the low volume (high pressure) end.

TABLE J-3. DETERMINATION OF P,G FROM THE PRESENT

U vs V CALCULATION

Volume (BM units)	P^a (Mbar)	PV (ev)	U (ev)	G (ev)
10.414	1.905	12.40	1.50	13.90
14.83	0.895	8.29	-2.07	6.62
17.45	0.523	5.67	-3.21	2.46
20.40	0.253	3.22	-3.90	- 0.68
23.55	0.132	1.935	-4.253	- 2.32
30.93	0.074	1.415	-4.702	- 3.29
35.20	0.057	1.260	-4.876	- 3.62
39.72	0.041	1.013	-5.015	- 4.00
55.81	0.010	0.342	-5.228	- 4.89
68.64	0.004	0.161	-5.284	- 5.12
76.63	~0.000	0.000	-5.293	- 5.29
83.31	-0.001[b]	-0.071	-5.290	
100.0	-0.002[b]	-0.120	-5.271	

[a]From DSPLSW 6/24/77
[b]Computed pressure is negative

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TABLE J-4.   DETERMINATION OF P,G FROM THE STEVENSON (ROSS) MIXTURE

U vs V PLOT (REF. 1)

| Volume | | P^a | PV | U | G |
(S units)	(BM units)	(Mbar)	(ev)	(ev)	(ev)
8.4	14.0	0.895	7.81	-4.01	3.80
8.94	14.85	0.802	7.43	-4.50	2.93
10.0	16.6	0.533	5.55	-5.24	0.31
11.25	18.7	0.374	4.35	-5.79	-1.44
12.5	20.75	0.319	4.14	-6.26	-2.12
15.0	24.92	0.124	1.925	-6.777	-4.85
17.5	29.07	0.0741	1.345	-7.026	-5.68
20.0	33.22	0.0527	1.092	-7.186	-6.09
25.0	41.53	0.0212	0.550	-7.384	-6.83
30.0	49.83	0.0068	0.210	-7.435	-7.23

[a]From DSPLSW 6/27/77

[1]D. J. Stevenson, Nature 258, 222 (1975).

Units Conversion:

atomic units ↔ cm³

$$\text{Volume} = \frac{4\pi}{3} (a \text{ in a.u.})^3 \left[\frac{0.52917\overset{\circ}{A}}{a.u.} \cdot \frac{10^{-8} \text{cm}}{\overset{\circ}{A}}\right]^3 ;$$

thus, volume (in $\frac{\text{cm}^3}{\text{N-atom}}$) = 0.62069 x 10^{-24} (a in a.u.)³,

or, volume (in $\frac{\text{cm}^3}{\text{N-atom}}$ x 10^{24}) = 0.62069 (a in a.u.)³.

or, $\frac{(\text{BM volume \#})}{0.62069}$ = (a in a.u.)³.

Stevenson (S) volume units ↔ Bernal-Massey (BM) volume units

$$\text{volume} = 10^{-24} (\text{BM volume \#}) \frac{\text{cm}^3}{\text{N-atom}} .$$

$$\text{volume} = (\text{S volume \#}) \frac{\text{cm}^3}{\text{mol NH}_4} .$$

$$10^{-24} (\text{BM vol \#}) \frac{\text{cm}^3}{\text{N-atom}} \left[\frac{6.02 \times 10^{23} \text{ N-atoms}}{\text{mol NH}_4}\right]$$

$$= 0.602 (\text{BM vol \#}) \frac{\text{cm}^3}{\text{mol NH}_4}$$

thus, the volume in S units = 0.602 (volume in BM units)

dU/dV ↔ P

$$\frac{dU}{dV} = \frac{\Delta(\text{BM U ev/N-atom})}{\Delta(\text{BM V x } 10^{-24} \text{ cm}^3/\text{N-atom})} \left[\frac{1.602 \times 10^{-12} \text{ erg}}{\text{ev}}\right]$$

$$\times \left[\frac{1 \text{ dyne-cm}}{\text{erg}}\right] \left[\frac{1 \text{ Mbar}}{10^{12} \text{dyne/cm}^2}\right]$$

$$= (\text{BM slope value})(1.602) \text{ Mbar};$$

thus, (1.602)(slope as from BM) gives P in Mbar, and (0.602)(1.602)

$\times$(slope as from Stevenson) gives P in Mbar.

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